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New Approaches Towards Novel Composite and Multilayer Membranes For Intermediate Temperature-Polymer Electrolyte Fuel Cells And Direct Methanol Fuel Cells

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Abstract

This review analyses the current and existing literature on novel composite and multilayer membranes for Polymer Electrolyte Fuel Cell applications, including intermediate temperature polymer electrolyte fuel cell (IT-PEFC) and direct methanol fuel cell (DMFC) systems. It provides a concise scrutiny of the vast body of literature available on organic and inorganic filler based polymer membranes and links it to the new emerging trend towards novel combinations of multilayered polymer membranes for applications in DMFC and IT-PEFC. The paper carefully explores the advantages and disadvantages of the most common preparation techniques reported for multilayered membranes such as hot-pressing, casting and dip-coating and also summarises various other fresh and unique techniques employed for multilayer membrane preparation.

Keywords: Intermediate Temperature Polymer Electrolyte Fuel Cells (IT-PEFC), multilayer membranes, DMFC, solution casting, dip coating, hot pressing.

Author Profiles

Miss Carolina Musse Branco graduated in Material Engineering at Universidade Federal do Rio Grande do Sul (Brazil) in 2011. There she continued her Masters on electrolyte polymer/cellulose membranes for PEMFC with hydrogen at Laboratorio de Materiais Polimericos. In 2013, she joined the Centre for Hydrogen and Fuel Cell Research at the University of Birmingham, UK, as a PhD student and is currently investigating multilayer membranes for intermediate temperature PEFC.

Dr Surbhi Sharma graduated in Physics from Delhi University (India) and completed her masters in Nanoscience from Amity University (India). She received her PhD from University of Ulster on the synthesis, characterisation of graphene oxide and the Pt-graphene oxide hybrids as catalyst-support systems for DMFCs. She joined the University of Birmingham in

2011. She has interests in the field of graphene oxide based materials for catalyst-supports, composite membranes for fuel cells and electrochemical biosensors.

Prof Maria Madalena C. Forte received her PhD in 1995 from the Institute of Macromolecules of the Federal University of Rio de Janeiro. Since 1997, she is professor at UFRGS in the Engineering School (Porto Alegre/Brazil). Prior to this, she worked at a Petrochemical Company for ten years. Dr Forte is Research Fellow of the Brazilian National Council in Research and a member of the Brazilian Association of Polymers and of Rubber Technology. Her current research interests are exploring polymers for fuel cell membranes.

Prof Robert Steinberger-Wilckens studied Physics with a specialisation in renewable energies; Ph.D. degree from University of Oldenburg (Germany) in 1993 with work on

integrating large scale renewable energies into the electricity grid. Founded engineering consultancy PLANET (Planungsgruppe Energie und Technik) in 1985. Involved in R&D in hydrogen, fuel cells and electric vehicles since 1997. Programme Manager SOFC at Forschungszentrum Jülich from 2002 and Chair for Fuel Cell and Hydrogen Research at University of Birmingham from 2012.

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1. Introduction

In the last few decades, the mounting concerns over environmental issues and a consequent bend of socio-economic policies towards greener alternatives have led to an extensive research into the development of fuel cell economy. Fuel cells are electrochemical devices that use hydrogen (or hydrogen based chemicals) as fuel, which combines with oxygen to produce electricity, water and heat. The hydrogen feeds the anode (where it is oxidized), producing protons and electrons in the presence of a catalyst (usually platinum). An electrically insulating electrolyte allows protons to pass through to the cathode and blocks the electrons, enabling a current flow in the external circuit. At the cathode electrons re-combine with the protons and the oxygen supplied at the cathode to produce water. The schematic of the well-known anodic and cathodic reactions in a fuel cell are shown in Figure 1a. The advantages of fuel cells over the existing fossil fuel based systems (internal combustion engines) are i) no generation of harmful, greenhouse gases like SO_x, NO_x, CO_2 and CO; ii) higher efficiency and iii) reduced sound pollution. However, drawbacks such as the high cost of component materials, storage and production of high purity hydrogen, scaling up and long-term durability and performance of the individual components as well as that of the system still remain to be addressed more effectively to enable large-scale commercialisation. [1-4]

There are many kinds of fuel cells, which operate on different fuels (acting as a source of hydrogen) and have varying operating temperatures, covering a whole range from 50 °C up to 1000 °C. Fuel cells are commonly classified on the basis of their electrolyte [5] according to which they can be divided into five main groups: Alkaline Fuel Cell (AFC), Phosphoric Acid

Fuel Cell (PAFC), Polymer Electrolyte Fuel Cell (PEFC), Molten Carbonate Fuel Cell (MAFC) and Solid Oxide Fuel Cell (SOFC). PEFC can be further sub-divided into three groups, the general PEFCs feed on hydrogen, Direct Methanol Fuel Cell (DMFC) and Direct Ethanol Fuel Cell (DEFC). Direct alcohol fuel cells (DMFC and DEFC) are similar to the PEFC in operation but as the names suggest, they feed on methanol and ethanol, respectively. PEFC (including DMFC and DEFC) are preferentially used in small devices and in transport applications that require quick start-up and do not require very high power. Among the various components of a PEFC is the proton exchange membrane (PEM) that plays the most vital role, i.e. separating the anode from the cathode, which enables the current flow through an external circuit. The performance of a PEM strongly affects the durability and efficiency of the fuel cell system. The most important properties required for an ideal PEM can, therefore, be outlined as (1) electrically insulating, (2) good proton conductivity, and (3) impermeable to gases and/or fuel to prevent gas/fuel crossover.

Proton exchange membranes are a sub-category of ion exchange membranes, which have been used quite successfully in diverse industries and applications (such as dialyses, electrolyser and desalination of water, among others) [6-8] before the advent of PEFC. Perfluorinated sulphonic acid (PFSA) polymers, usually fluorinated copolymers of tetrafluorethylene-co-sulphonic acid monomers with high thermal and chemical stability, are the most successfully used commercial membranes for PEFC and alcohol fuel cells. The PFSA membranes have two phases: a hydrophobic phase consisting of tetrafluorethylene (PTFE) forming the backbone (Fig.1b, block m) which provides mechanical resistance, and a hydrophilic phase consisting of side chains having sulphonic acid group (Fig.1b, block n) which is responsible for the proton transport. [9, 10] The proton conductivity is due to the

main carbon chain, which separates the side chains, thus forming the polar and non-polar regions. Proton transport through the electrolyte membrane can occur by the Grotthuss (also called hopping mechanism) and vehicular (diffusion) mechanism. [10, 11] According to the Grotthuss mechanism, protons that are linked to the sulphonic groups combine with water molecules in the hydronium (H_3O^+) form. A proton of the hydronium is then transferred to another water molecule bonded to a nearby sulphonic acid group (see Figure 1c), and these water molecules form the 'Water Bridge'. Thus, the proton hopping occurs through the network of hydrogen bonds. Higher the water molecule content attached to sulphonic acid group (λ), closer the water molecules are to each other, resulting in faster proton transport (facilitated between the $-SO_3^-$ groups) through the membrane. The λ is defined as the number of water molecules per sulphonic acid group. On the other hand, according to the vehicular mechanism, proton in the hydronium H_3O^+ ion, due to electrochemical differences diffuses with water molecules through the membrane. [2] Although it is possible that both mechanisms are active simultaneously, Grotthuss mechanism is considered to be the preferred and faster mechanism. [12, 13]

The most successful commercial PFSA membrane is Nafion®, developed in the early 1970s by DuPont. Chemical structure of Nafion® consists of PTFE sequences without and with side chains of perfluoroether, that end in sulfonic acid groups ($–SO_2OH$) (as the fluoro 3,6-dioxo 4,6-octane sulphonic acid shown in Fig.1b). Other companies also made their own Nafion-like membranes, such as Flemion® from Asahi Glass Company Ltd and Dow membrane, from Dow Company. [2] Nonetheless, in spite of the extensive studies on polymer membranes to substitute Nafion, no reported membrane has so far achieved a performance comparable to that of Nafion in PEFC. Although, some other membranes may exhibit certain proprieties

better than Nafion, so far none seem to have the optimum balance between all the properties that is demonstrated by Nafion®. However, Nafion® still suffers from various drawbacks like degradation due to dry conditions during start stop cycles, and due to fuel crossover, especially in DMFC systems, leading to loss of cell performance as revealed by various long-term studies. Moreover, recent studies [14-16] investigating performance of membranes in intermediate temperature (100 to 120 °C) PEFC (or IT-PEFC), suggest the need to develop new membranes which could solve specific problems faced by PEMs in this kind of environment. Operating at higher temperatures not only enables faster reaction kinetics for hydrogen oxidation and oxygen reduction but also a) enables better catalytic activity due to reduced poisoning from CO and other gases and b) facilitates easier water management and elimination. [17] However, the operation of IT-PEFC at temperatures between 100-120 °C means the PEM needs to be more tolerant, especially towards low humidity conditions, in order to maintain proton transport and prevent membrane degradation. [18, 19] While proton transport in hydrated membrane is commonly explained through the formation and cleavage of hydroniums bonds, thermodynamically this route is not the most favourable. There are two widely accepted structures involving the hydronium: the Zundel ($H_5O_2^+$) cation and Eigen ($H_9O_4^+$) cation complex (Figure 1d). In the Zundel $H_5O_2^+$complex, two water molecules in symmetric hydrogen bond share the proton equally. In the Eigen solvated structure, the hydronium ion is at the centre of the $H_9O_4^+$ complex and is strongly bonded to three neighbouring water molecules via hydrogen bonds. [20] Both complexes represent the ideal structures in a more general hydrogen bond network and define the diffusion of the hydrogen-bond structure in which the excess proton is transported/tunnelled back and forth. It is thought that both the complexes transform into each other and act as donors of protons by the formation and cleavage of hydrogen bonds.

These bonds are not as strong as those in simple hydronium structures and therefore enable a faster proton transfer. [20]

Proton diffusion, although independent of transport mechanism, increases as temperature and membrane hydration level (λ) increase. Feng and Voth [21] in a modelling study investigating transport of protons have revealed that for λ values between 6 and 15 and for temperatures between 25 °C to 67 °C, the Grotthuss mechanism has a higher diffusion ratio than that of vehicular mechanism. As the temperature and value of λ increase, Grotthuss mechanism becomes more dominant. The activation energy available for proton transport drops for λ values less than 10 due to the different solvation structure at this level of hydration. Beyond this exception, the activation energy increases with λ being almost the same as in pure water when λ is 15. The indispensability of water to proton transport, as established by the various proton transport and diffusion mechanisms, underlines the importance of incorporation of hydrophilic groups in Nafion or any other PEMs to enable higher proton conductivity especially at elevated temperatures. Therefore, if a hydrophilic group is added, the water retention would improve resulting in better proton conductivity. This is the concept behind all composite membranes. Another new concept under investigation to achieve better PEMs, is the use of multilayer membrane. A multilayer design can bring together layers of different polymers each bringing its unique characteristic (mechanical strength, non-permeability, better water retention, etc.) property to the composed multilayer membrane, eliminating the need for compromising one property for another when choosing a PEM material.

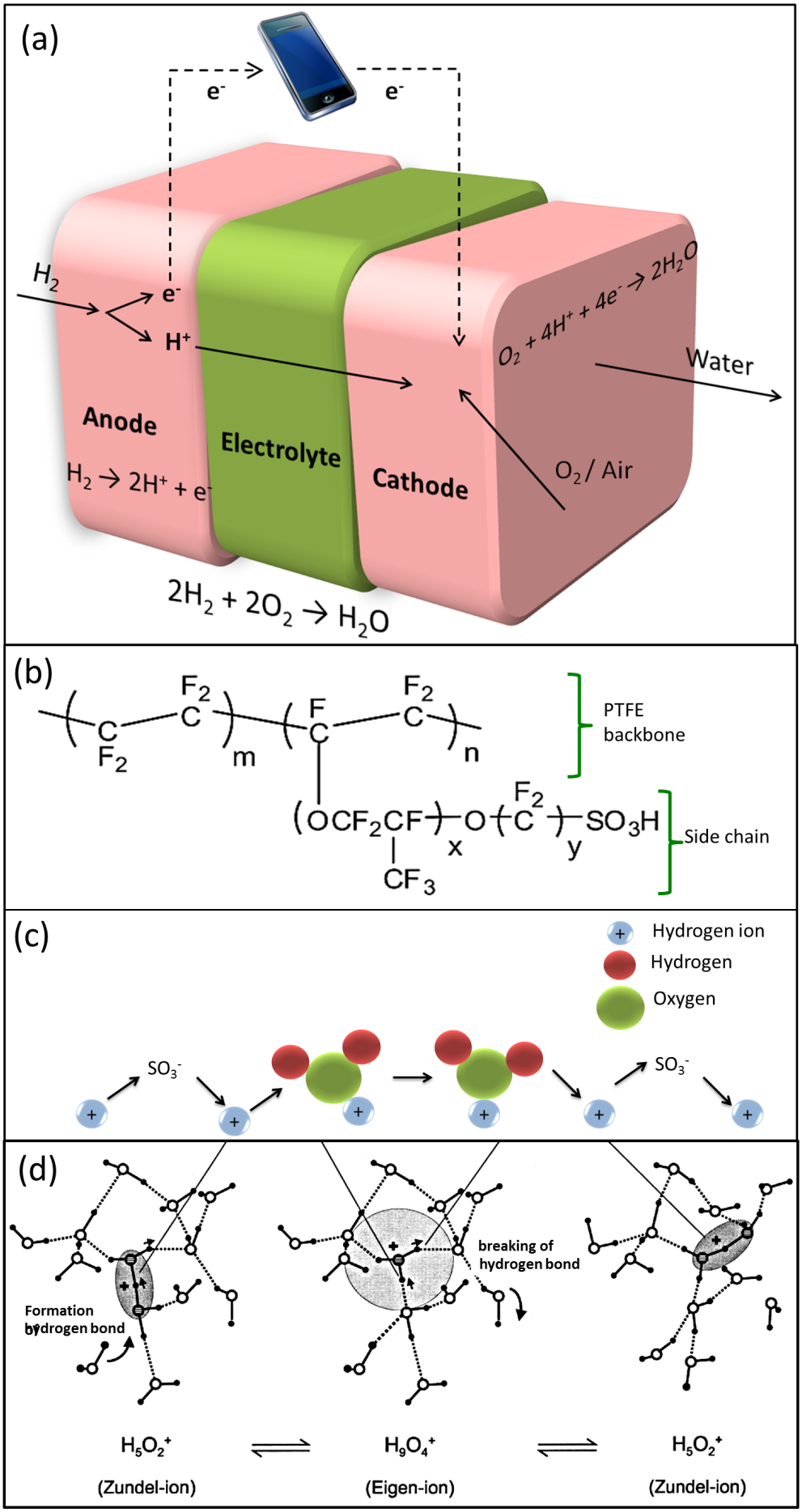
(a)
e⁻
e⁻
H₂
e⁻
H⁺
Anode
H₂ → 2H⁺ + e⁻
Electrolyte
Cathode
O₂ + 4H⁺ + 4e⁻ → 2H₂O
Water
O₂ / Air
2H₂ + 2O₂ → H₂O
(b)
PTFE backbone
Side chain
(c)
Hydrogen ion
Hydrogen
Oxygen
SO₃⁻
SO₃⁻
(d)
Formation of hydrogen bond
breaking of hydrogen bond
H₅O₂⁺
(Zundel-ion)
H₉O₄⁺
(Eigen-ion)
H₅O₂⁺
(Zundel-ion)

Figure 1: (a) Schematic of the anodic and cathodic reactions in a typical fuel cell. At the anode, hydrogen is oxidized yielding electrons that move through the external-circuit providing energy to the device, and protons that are transported through the electrolyte. At the cathode, both react with oxygen producing water. (b) Nafion chemical structure [137] and (c) Schematic of Grotthuss mechanism scheme showing the proton movement between sulphonic acid groups in the hydronium form. (d) Zundel-ion and Eigen-ion structures showing the formation and cleavage of hydrogen bonds for the protons transport in a hydrated membrane. [20]

This review focuses on the new developments in composite and multilayer membranes for IT-PEFC and DMFC, highlighting the various unique and novel approaches towards multilayer membrane development. The composite membranes section covers both organic and inorganic filler membranes. However, since membranes with organic fillers have been extensively discussed in previous works [22-25], this paper highlights only the more recent work on organic fillers and provides a more detailed discussion on inorganic fillers. This is followed by extensive analysis of the recent reports on multilayer membranes for use in IT-PEFC and DMFC, speculating the future possibilities due to this paradigm shift in our perspective of PEMs.

2. Composite membranes

Polymeric composites are materials with a polymeric matrix and a filler or reinforcement, which can be another polymer, ceramic or metal. The fillers used in PEM usually are ceramic or polymeric. The two components must have separate phases. The filler is used to improve one or more polymer proprieties or reduce the material costs. The routes to produce composite polymer membranes are similar to any other composite polymer.

However, composite membranes can be considered as one of the first attempts to develop something better and challenge the existing industry standards. The advantage of the use of composite membrane over blend membranes is that the proprieties of the filler and matrix are preserved and can give other characteristics that are not possible with blend membranes. Sulphonic acid groups are highly hydrophilic and for this reason many polymers are commonly sulphonated. Numerous studies have been reported on Nafion and other sulphonated polymers with the aim of improving the PEM properties such as mechanical resistance, proton conductivity, chemical and thermal stability, water up take etc. [2, 12, 26-31] Some of the aspects analysed have been inorganic fillers, cross-linked polymers, use of alternative solvents during membrane casting etc. A selection of these approaches is briefly discussed here. Donnadio*, et al.* [32] developed a sulphonated poly(ether sulphone) (SPES) membrane with 34% degree of sulphonation (DS), and zirconium phosphate as filler. Their results revealed a maximum membrane conductivity of $4.5x10^{-2}$ $S.cm^{-1}$ at 100 °C and 90% relative humidity (RH). The authors found the conductivity of the membrane to be very stable up to 120 °C at 75% RH. The conductivity values for the SPES membrane, however, were found to be lower than that of Nafion 117. Park*, et al.* [33] prepared a cross-linked sulphonated poly (arylene ether sulphone) (SPAES) membrane for DMFC application. Their crosslinked SPAES membranes revealed less water uptake, lower methanol permeability and good mechanical and thermal strength compared to non-crosslinked membranes. Single cell DMFC testing of the membranes showed a performance similar to that of Nafion 115. Jun*, et al.* [34] prepared a sulphonated poly(ether ether ketone) (SPEEK) membrane and analysed the effect of different polymer solvents on the resultant cast membrane for use in PEFCs. For the solvents, the authors used N-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc) and dimethylformamide (DMF) and observed that the cast

membrane prepared with NMP as the solvent showed a performance similar to that of Nafion 117. With this study, the authors brought to light the importance of the choice of casting solvent as well as the membrane activation treatment in determining the performance of a cast membrane. Silva*, et al.* [35] used a sulphonated poly (styrene-*co*-acrylonitrile) membrane as PEM. Although, the studies mentioned above contributed towards understanding the behaviour of proton transport through a sulphonated polymer, the sulphonated polymers or their blends usually did not achieve all the Nafion characteristics. This has led to the investigation of composite membranes that could be loaded with fillers in order to upgrade a given property such as mechanical resistance, proton conductivity, water uptake, gas barrier or reduced fuel crossover and stability. In the case of the IT-PEFC, the use of composite membranes could also help avoid Nafion degradation during operation at elevated temperatures.

Composite membranes can be loaded with organic or inorganic fillers. Some of the organic fillers are the reinforcement polymer fibres or particles such as PTFE. Inorganic fillers are metal oxides and carbon based materials. Both inorganic and organic fillers have been used predominantly to increase proton conductivity and to act as a barrier to the gases. The following sub-sections concisely discuss the latest developments in the organic and inorganic filler based membranes.

2.1. Organic fillers

Organic materials are commonly used fillers in the polymeric composite membranes for FCs. They supply reinforcement and allow higher stability of the matrix polymer while making it more cost effective. The most commonly applied organic filler is PTFE fibre reinforcement.

For example, Wang *et al*. [25] reported the membrane preparation of sulphonated polyimide matrix. However, recent investigations show more inclination towards using inorganic or organic/inorganic fillers in polymeric composite membranes which have been discussed extensively in previous reviews by Li*, et al.* [36], Ahmed and Dincer [37] and Li*, et al.* [38]. As such our discussion on organic fillers here has been kept concise and limited to only recently reported studies on this subject. The development of organic composite membranes using a porous sheet with the conductive polymer solution has also been reported in the literature. [22, 24] Wu *et al.* [22] studied the accelerated stress degradation of the MEA in a PEFC where the PEM was a porous PTFE support impregnated with Nafion solution. In a similar way Lu *et al.* [24] prepared a membrane with porous PTFE support impregnated with a solution of poly(ethersulphone)-poly(vinylpyrrolidone) (PES/PVP) and doped further with phosphoric acid. Figure 2 shows the cross sections of the membranes with different amount of PTFE as prepared by the authors. In this case, the (PES/PVP) formed the hydrophilic phase, which provides the proton conductivity, while the (PTFE) formed hydrophobic phase providing mechanical resistance and structure to the membrane. The authors found that the PEFC performance at 150 °C was considerably superior after the PTFE reinforced membrane and the best result was obtained at 180 °C with a 3% PTFE membrane without any humidification. A particular problem in this kind of membrane preparation is the low compatibility of the PTFE and PES/PVP due to the hydrophobicity of the fluorinated polymer. However, doping the membrane with phosphoric acid is reported to improve the interaction between the polymers. Although this membrane is not labelled as a multilayer membrane, this work can be seen as a transitional study between composite and multilayer membranes.

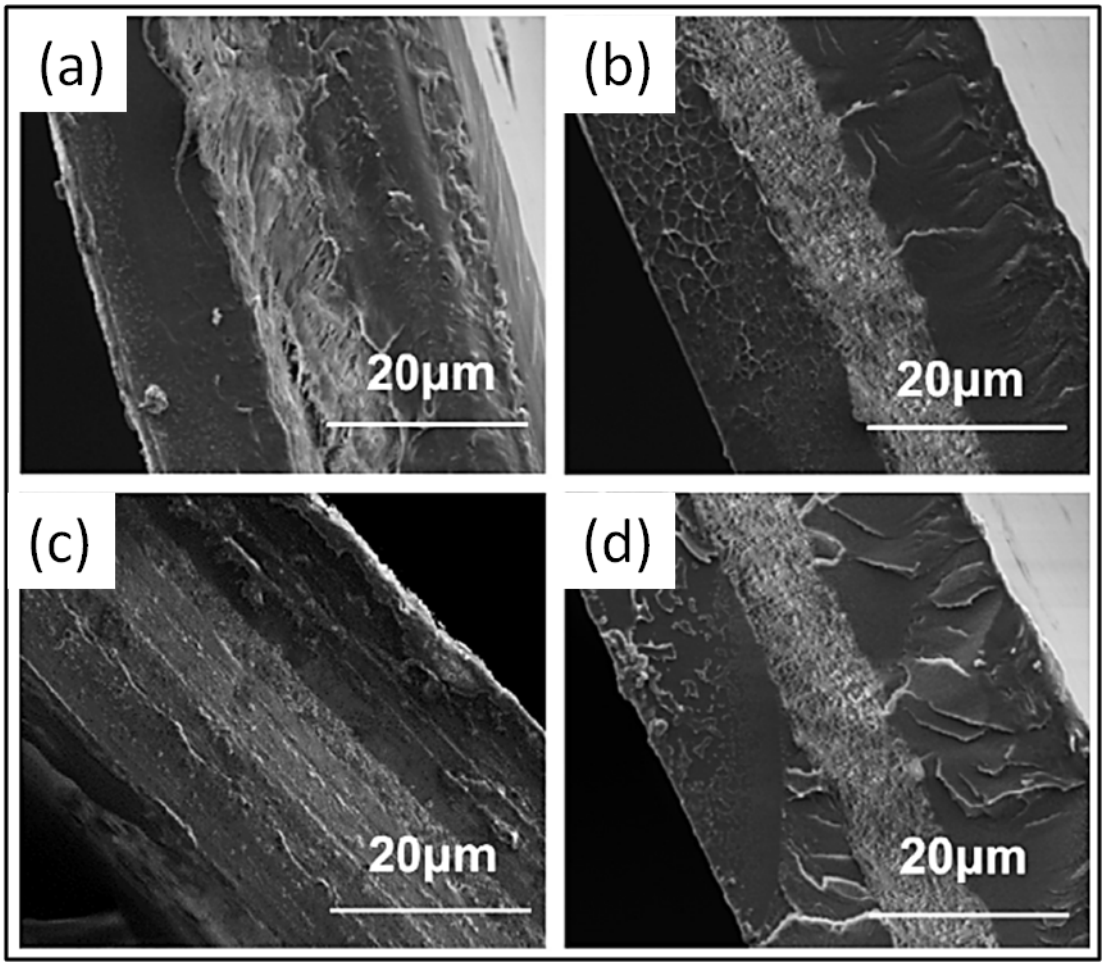

Figure 2: SEM micrographs of the PES/PVP membranes (a) without, with (b) 3%, (c) 5% and (d) 7% of PTFE. [24]

Organic composite membranes have also been used in DMFCs. In a recent study, Alvarez*, et al.* [39] used polyamidoamine dendrimers as fillers in Nafion matrix with the aim to avoid methanol crossover. Methanol crossover is one of the major issues affecting long-term performance of the DMFC system, as it leads to cathode catalyst poisoning and consequent drop in OCV values. The investigations by Alvarez *et al.* [39] revealed that the methanol crossover was lower in the composite membrane when compared to recast Nafion in a DMFC single cell system operating at 100 °C with 2 M methanol. In another study, Lin*, et al.* [40] evaluated porous PTFE impregnated Nafion membranes for use in DMFC. The single cell test was carried out at 70 °C with 2 M methanol for Nafion 117, Nafion 112 and PTFE/Nafion

membranes. The data revealed that the power density as well as the current density was considerably higher (5 mW cm^{-2}, 350 mA cm^{-2}) for the polarisation studies carried out using composites membranes than those with Nafion membranes. The authors emphasised that even with lower proton conductivity than Nafion, the performance of the PTFE impregnated membranes was superior to that of Nafion because of the PTFE's ability to reduce the methanol crossover and minimise further degradation of the membrane.

Lin and Wang [41] prepared a composite membrane for DMFC which was composed of a porous thin film of crosslinked poly(vinyl alcohol) (PVA) nanofiber impregnated with Nafion. The conductivity of the composite membrane was found to be lower than that of Nafion membranes, because, similar to PTFE, PVA is a non-conductive material. Furthermore, similar to the results for PTFE impregnated Nafion membranes, the voltage data obtained in a DMFC single cell operating with 2 M methanol with Nafion PVA impregnated membranes were superior to that of Nafion 117, 212, and cast Nafion membranes. Here again, it is the reduced methanol crossover (Table 1), which enables better membrane performance in the DMFC environment. Due to the unique membrane microstructure of PVA nanofibers, it offers increased tortuosity making it difficult for the methanol molecules to crossover.

Table 1: MeOH permeability data of Nafion 117, 212, cast Nafion and Nafion/PVA membranes [41].

Membrane	**P (10^{-6} cm^2 s^{-1})**	**p = P/L (10^{-4}cm s^{-1})**
C_a = 2M (6.41 wt%)		
Nafion – 117	4.20 ± 0.09	2.4 ± 0.05
Nafion 212	4.73 ± 0.06	9.4 ± 0.1
Nafion – cast	5.09 ± 0.07	9.84 ± 0.02

N/VA-f-9.5-0.5	3.47 ± 0.07	6.6 ± 0.1
N/VA-9-1	2.83 ± 0.05	5.7 ± 0.1
N/VA-f-8-2	2.74 ± 0.09	5.3 ± 0.2
N/VA-b-9.5-0.5	4.11 ± 0.09	8.4 ± 0.2
N/VA-b-9-1	3.22 ± 0.05	6.2 ± 0.1

Organic composite membranes have been reported in the literature since the earliest papers about PEM. [36, 42] These early studies have already suggested that inorganic-organic composite membranes should be the approach in the future. Especially, since most of investigations on organic composites use PTFE as filler or matrix. As seen in the papers discussed above, PTFE is a hydrophobic, ionic insulator. As such, it is expected neither to improve the proton conductivity nor to enable better water retention at high temperatures. It only acts as a barrier to reduce the fuel crossover enabling improved PEM efficiency in DMFC, DEFC which is subject to standard PEFC conditions only. However, some inorganic filler are capable of providing a barrier as well as increase the proton conductivity. Consequently, this has generated more interest in inorganic fillers and this shift in trend can be seen from the large number of studies published focussing on this subject over the last few years.

2.2. Inorganic fillers

Inorganic nanoparticles provide many advantages when added to a polymeric matrix due to their different nature providing new properties to the composite, especially improving mechanical strength. The variety of fillers can be divided into categories based on the

properties offered by them or according to the type of materials. Zhang and Shen [12], in a detailed review on polymer electrolyte membranes, classified the inorganic fillers used in composite membranes into three categories: i) inert hygroscopic, ii) proton conductivity, iii) hydrophilic and proton conductivity. The inert fillers in the first category are used specifically to decrease the fuel crossover and hold water. As they are hygroscopic, the water molecules are adsorbed onto them even under high temperature and low humidity conditions. These kinds of fillers may not always enable higher conductivity. The second category includes the fillers with high elastic modulus because of which they assure higher proton conductivity. In the third category, fillers are both proton conductors and hygroscopic, and usually are sulphonated hygroscopic materials from the first group. Most of the literature reports are particularly focussed on the groups i and iii. This review categorises the fillers based on the material used, and are classified into two categories, namely i) metal oxides; and ii) carbon nanostructures. The metal oxides are inert hygroscopic materials, as in the first category of Zhang and Shen [12], and are the most extensively used materials as fillers in fuel cell membranes. The second category of fillers can be further sub-divided into two groups based on the nanostructure of the carbon material: a) carbon nanotubes; and b) graphene oxide. These two carbon nanostructures have been actively investigated in their native as well as various chemically modified forms due to their unique structural and chemical properties.

2.1.1. Metal oxides

Certain hydrophilic metal oxides are known to increase the water up-take of PEM significantly, which facilitates the proton transport via Grotthuss mechanism. Among the metal oxides, one of the most widely researched materials is silicon oxide. Other common metal oxides used for this purpose include TiO_2 [43, 44], ZrO_2 [45] and Fe_3O_4 [46]. Adjemian,

et al. [47] introduced hydrated SiO_2 (via sol-gel method) in the Nafion hydrophilic channels to improve the water retention for use in a PEFC above 100 °C. The authors reported that under high humidity conditions, the power density and voltage of Nafion based system was higher than when composite membrane was used. However, under low humidity condition better performance was achieved with SiO_2/Nafion membrane (with 6 wt.% of SiO_2), which was attributed to the higher water uptake of the membrane due to the presence of SiO_2. However, the SiO_2/Nafion membrane did not display the same stability as the Nafion membrane and when the long-term performance was compared, the composite showed poor performance under all tested conditions. In another study, Ke*, et al.* [48] have prepared Nafion/SiO_2 composite membranes using an in-situ sol-gel method to achieve better size control over the SiO_2 nanoparticles. They performed studies with SiO_2 nanoparticles of 4 different sizes and reported that between 5-15 nm diameter particles, 10 nm SiO_2 particles resulted in the best performance in comparison to unmodified Nafion at high temperature (110 °C) and at low humidity (59% RH). This study however, did not look in to the long-term durability of the composite membrane. Kim*, et al.* [49] used silica with other polymers (sulphonated urethane acrylate-*co*-styrene and sulphonated polyimide) to obtain membrane for PEFC studies using a new preparation method, i.e. in-situ surface grafting reaction of reactive dispersion of silica nanoparticles to obtain better nanoparticle dispersion even in higher concentrations. In another study, Thiam*, et al.* [50] used Pd-SiO_2 nanofibers as filler in order to decrease methanol permeability of Nafion membranes for DMFC use. As SiO_2 is a hygroscopic material, when added in a polymer matrix, it holds water especially in low humidity conditions, and consequently these membranes show superior performance under extreme conditions. Pd being an electrochemical catalyst would enable the oxidation reaction in the presence of diffused methanol in the PEM, generating water

that would then be adsorbed by the silica fibers, thus facilitating self-humidification. Here the size of the silica supported Pd nanofibers ranged from 100-200 nm and the authors reported that a filler loading of 3 wt.% Pd-SiO_2 was the optimum value to achieve improved proton conductivity and reduced methanol permeability. Various other studies [51, 52] have also reported the inclusion of metal catalyst nanoparticles in the membrane for the purpose of self-humidification. While the concept is interesting, without long term tests it is difficult to establish that oxidation reaction inside the membrane does not lead to any peroxide (H_2O_2) formation which is known to cause membrane degradation in the presence of catalyst nanoparticles. [53, 54]

Devrim [55] has developed a composite membrane of Nafion/TiO_2 (with upto 10 wt.% of TiO_2 filler) and deposited the catalyst ink by ultrasonic solvent coating to test the MEA in-situ. Interestingly, the authors found that the water uptake, unlike some other fillers, was reduced in case of this composite membrane. The author attributed this behaviour to the interaction between the hygroscopic TiO_2 and the hydrophilic fraction of Nafion because of which the sulphonic groups could be hidden and would therefore be unable to adsorb sufficient amount water. This was further confirmed by the author's experiments where at 25 °C Nafion membranes presented high conductivity but the conductivity decreased as the amount of TiO_2 was increased. While, at higher temperatures (50 to 90 °C) the study revealed lower proton conductivity for the Nafion membrane than with the composites membranes, it was found to decrease as the TiO_2 content increased from 2.5 to 10 wt.%. The author hypothesised that even though the water uptake for the composite membranes was lower due to the TiO_2 – Nafion interaction, the TiO_2 was still able to hold water at higher temperatures. However, as the filler loading increased, an excess of TiO_2 would mask

the SO_3H groups completely. The composite membranes were further tested in a single cell PEFC and compared with solution cast Nafion. The author evaluated the cell performance at 80 °C, looking at various ratios of the inorganic filler. He also studied in detail the 2.5 wt.% TiO_2 system at various operating temperatures and the effect of the amount of TiO_2 on cell performance at low humidity (80 °C, 50% RH). The best cell performance was found for the 2.5 wt.% of TiO_2 at 80 °C and the worst performance for 110 °C. The I-V curves from the study revealed that the loss of water led to the performance being compromised even if the proton conductivity is higher at higher temperatures. Possible agglomeration of TiO_2 at higher loadings was also suggested to adversely affect the cell performance.

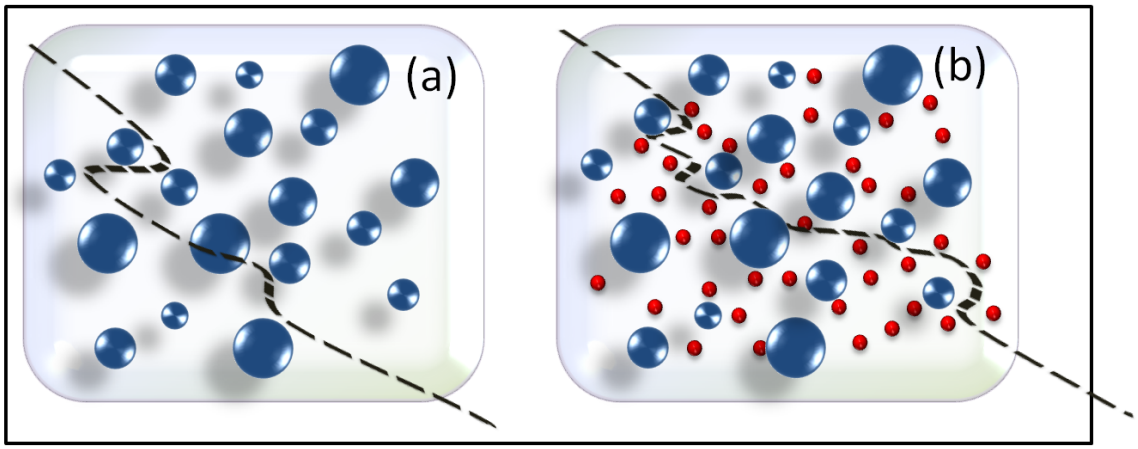

Figure 3: Schematic representing the fuel path (dashed line) in (a) the membrane with no filler and (b) the composite membrane with the filler particles (small red circles).

In case of membranes used in DMFC systems, the addition of silicate nanocompounds have been commonly used [56-58] to considerably reduce the amount of methanol crossover, since it is one of the major issues affecting long-term performance. The addition of silicates increases the tortuosity of the membrane, decreasing methanol permeability, following the Nelson Law (Equation 1).

$$\tau = 1 + \left(\frac{L}{2D}\right)\emptyset \qquad \text{(Eq. 1)}$$

Where τ is the tortuosity factor, L is the length and D is the width of silicate layer and $\emptyset$ is the volume of silicate in the polymer matrix. [31] However, the silicates act as physical barriers to water molecules too. The path that the fuel must follow through the membrane is considered to be longer in the presence of these particles (Figure 3). The longer, zig-zag path which the methanol must follow in the composite membrane slows down the rate of crossover, increasing the durability of the membrane and the DMFC. Methanol crossover causes more serious problems than hydrogen crossover. Therefore, standard commercial membranes used in DMFC are thicker than those in PEFC in order to reduce the crossover of methanol. This use of thicker membranes also makes it easier to use silica fillers for the composite membranes used for DMFC. However, the concept of increasing tortuosity by adding filler nanoparticles can still be applied to PEFC using other filler materials. Although, it is important to note that H_2 crossover will not be affected as significantly as methanol crossover, since the hydrogen molecule it is a much smaller molecule.

Since inorganic/polymer composite membranes are able to operate at higher temperatures as compared to polymer membranes, other metal oxide particles have also been keenly investigated. Devrim*, et al.* [59] developed a nanocomposite membrane with 10 wt.% titanium silicon oxide ($TiSiO_4$) and Nafion for use in PEFC. The authors pointed out that the distribution of $TiSiO_4$ and its interaction with Nafion were extremely good. The authors suggested that the chemical and electrostatic interactions between Nafion sulphonic groups and the nanoparticles enabled the orientation of the polymeric molecules around the inorganic nanoparticles facilitating homogeneous distribution of the nanoparticles in the membrane. $TiSiO_4$/Nafion was found to show higher proton conductivity at temperatures

above 55 °C and higher water uptake above 30 °C compared to the solution recast Nafion. The increase in proton conductivity was attributed to the significant increase in water uptake at higher temperatures (below 100 °C). The performance in a PEFC prototype at 85 °C was also reported to be better with the composite membrane than with Nafion. The peak power density was also reported to be higher, i.e. for 0.8 $A.cm^{-2}$, the power density for 2.5 wt. % of TiO_2 was reported as 0.4 $W.cm^{-2}$ while for Nafion it was reported as 0.25 $W.cm^{-2}$. The authors claimed that the higher performance and slower degradation was achieved due to the addition of the oxides. Mishra *et al.* [44] synthesised TiO_2 nanoparticles via sol-gel to use as filler in sulphonated PVA membranes for PEFC and DMFC. In this study the effect of process variables within the sol-gel preparation method on the nanoparticle size and aggregation was investigated. Titanium dioxide, as for most inorganic oxides, is used as filler for the same reason as SiO_2. The differences are in the specific characteristics, such as the conductivity, size or dispersion ratio of each type of filler, which influence the amount of inorganic material that must be loaded. Factors like nanoparticle size distribution and aggregation behaviour are extremely important and play a strong role in determining the performance of the final composite membrane. Whilst the nanoparticle size and distribution would be strongly affected by the parameters used as well as the synthesis method employed, the aggregation behaviour will be affected by the nanoparticle-polymer interaction and hence even for the same filler nanoparticle would vary from one polymer to another. However, very few studies have actually investigated these essential aspects in composite membrane behaviour.

Sangeetha Rani*, et al.* [60] prepared a composite membranes with zirconium titanium phosphate (ZTP) loaded in a SPEEK matrix for DMFC. The authors investigated the effect of

ZTP loading (5, 10 and 15 wt.% of ZTP loading) and noticed that the ion exchange capacity (IEC) increased with increase in loading up to 5 wt.% of ZTP, beyond this loading the IEC was reported to decrease and the loss in IEC was attributed to the strong interactions between the sulphonic acid groups of the polymer and ZTP. While IEC is a commonly used ex-situ characterisation technique for fuel cell membranes, the huge difference in the *in-situ* single cell and *ex-situ* test conditions means that the test does not always provide the most accurate results when compared to *in-situ* I-V or even proton conductivity. The test, however, can help provide insight into various possible mechanisms which could be responsible for PEM behaviour under given conditions. The authors also reported that the water uptake decreased as the loading of ZTP increased, and it was found to be even lower than that of SPEEK without any filler. This low water uptake was also attributed to the strong interactions between the matrix and the filler. This case is different from the oxides discussed above, as ZTP is not a hygroscopic compound but offers higher proton conductivity.

As the oxides do not necessarily achieve satisfactory proton conductivity, one commonly used solution to overcome this is to functionalize these materials with specific groups that may increase the conductivity. The most commonly reported method for filler functionalization is to incorporate sulphonic groups because these are extremely hydrophilic. These groups enable water retention especially under high temperature and low humidity conditions. Zhai*, et al.* [61] prepared sulphonated zirconia (S-ZrO_2) and used it as a filler in Nafion membranes for PEFC application. The amount of S-ZrO_2 filler used was varied from 0 to 20 wt. %. The authors found that the IEC values increased with the increasing ratio of S-ZrO_2 due to addition of acid points via sulphonic groups. The water

uptake was reported to be the highest for 10 wt.% of S-ZrO_2. Tests in PEFC prototype at 80 °C and 120 °C revealed that performance of 15 wt.% S-ZrO_2/Nafion (reported as the optimum ratio) membrane was slightly better than that of commercial Nafion, and at 120 °C the difference in the performance of the optimised composite and commercial membranes was quite significant due to the increased retention of water in the presence of S-ZrO_2. The authors found that above this loading (15 wt.%) of S-ZrO_2 in the composite membrane, the performance was always lower than that of the commercial membrane. Wu and Scott [43] went one step further with TiO_2 fillers and sulphonated titanate nanotubes (TiO_2-NT) to achieve higher water uptake and proton conductivity. The single cell PEFC testing revealed an impressive power density, which was four times higher than when using Nafion. Sulphonation of oxide fillers has revealed itself to be a simple and fast solution to improve proton conductivity for PEM. For most oxides, the process of sulphonation is well known making it a convenient and promising approach to use for preparation of composite membranes in PEFC and DMFC at high temperatures and low humidity.

Although, the use of metal oxides as filler has enabled many advantages towards improving the PEM, they too have some problems associated with them. The metal nanoparticles are often very difficult to disperse homogenously in the polymer membrane, which is dependent upon their interaction with the polymer. Variable dispersion of the metal nanoparticles in the membrane matrix would mean that the performance of the composite will not be uniform throughout the bulk of the membrane. Also, the metal oxides inside the PEM has the potential to accelerate the oxidation and rate of membrane degradation over time and more long-term, durability type studies are required in this direction to understand the actual benefits and drawbacks of these fillers. Consequently, carbon

nanomaterials have gained attention as they present high surface area, are inert and can be functionalized in different ways.

2.1.2. Carbon Nanomaterials

Besides the metal oxides, some carbon nanostructures have attracted a lot of interest as filler materials for composite PEMs over the past decade as these structures impart excellent proprieties to the membranes like i) increased the chemical resistance, ii) reduced the fuel crossover, iii) higher the thermal and mechanical resistance, and iv) potential increase of the proton conductivity depending on the structure. Moreover, unlike metal oxides the loading of carbon nanomaterials required for achieving the desired membrane performance is much lower when compared to the metal nanoparticle loadings used. In principle, the lower weight of the filler nanomaterial would also allow easier uniform dispersion.

Carbon Nanotubes

Carbon nanotubes (CNT), are sheets of graphite wrapped as tubes. They have been used very successfully in polymeric composites over the last 10-15 years. [62-64] CNTs boast of excellent mechanical proprieties due to the tube chirality. [65] The use of CNTs as fillers in PEMs has gained a lot of momentum in the past decade. Kannan*, et al.* [66] modified CNTs with phosphonic groups for use in PEFC. The CNTs were used as filler for a matrix of phosphoric acid doped poly(benzimidazole) (PBpNT) and was phosphonated in two steps. The authors claim that the stronger hydrogen bond between the phosphonic groups and water molecule leads to higher proton conductivity. The mechanical resistance was also reported to have increased due to the higher mechanical strength of CNTs compared to the polymer matrix. On testing the membrane *in-situ*, (Figure 4a) the authors affirmed that an

improvement of 40% in the cell performance was observed when using the composite membrane due to the improved interface between the electrolyte and the catalyst. The PBpNT structure can be seen in the Figure 4b. The dark lines represent the Nafion membrane, the blue circles are the phosphonic groups bonded to CNT, and the green circles are the phosphoric acid used to dope the membrane.

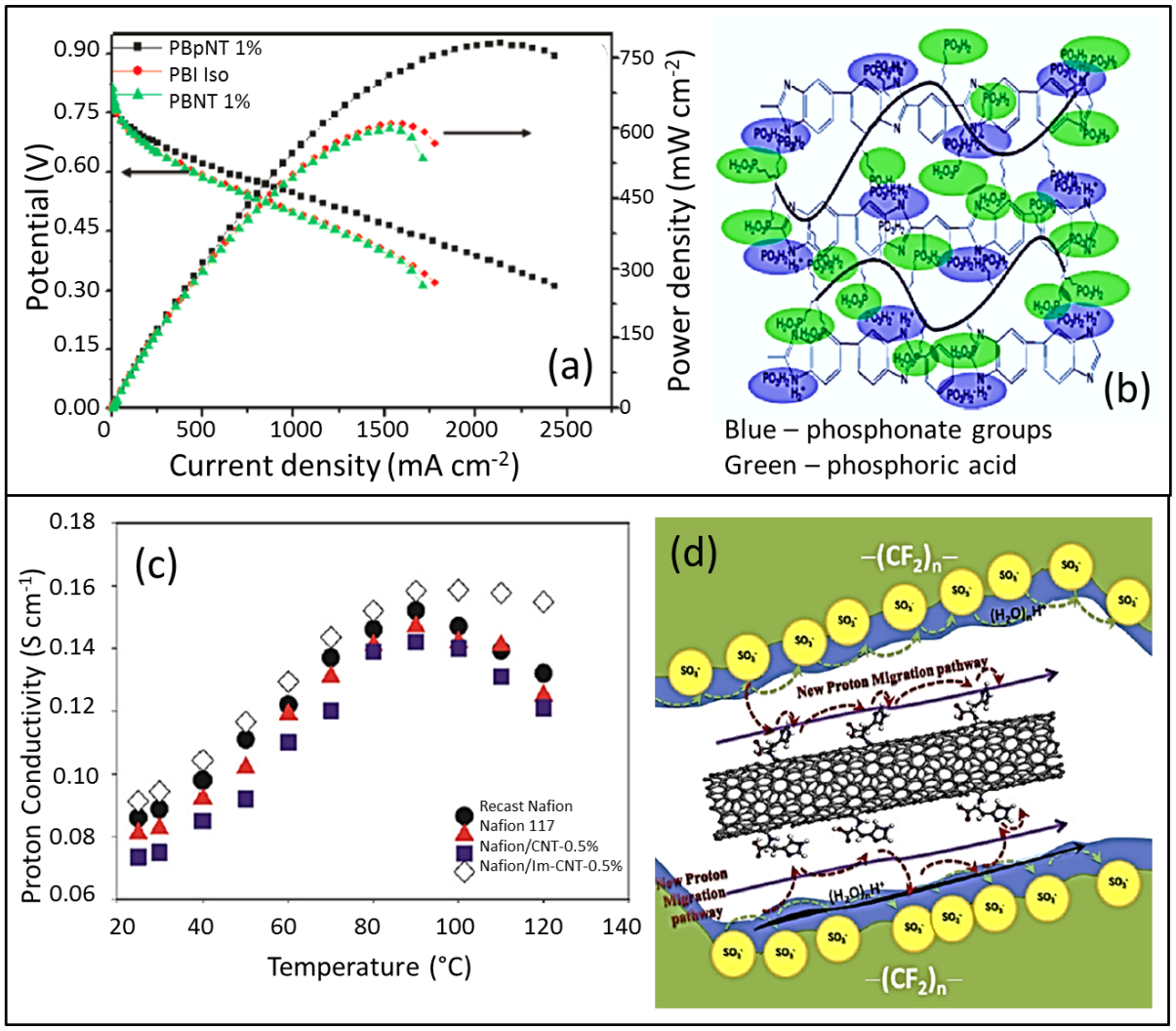

Figure 4: (a) Potential and power density vs current density obtained in a PEFC at 140 °C feed with H2 and O2 using a well-ordered (PBI Iso) and 1 wt.% CNT filled poly(bezimidazole) membrane, undoped (PBNT 1%) and doped (PBpNT 1%) with phosphoric acid. (b) Schematic illustration of the PBpNT membrane showing the PBI structure and phosphoric and phosphonic groups [66] (c) Proton conductivity of the composite and the recast Nafion membranes at different temperatures. (d)

Schematic illustration of the Nafion/CNT doped with Imidazole membrane, in which is possible to note the new path for the proton transport via Grotthuss mechanism. [67]

CNTs have also been commonly used in DMFC membranes. In one study, Asgari*, et al.* [67] developed a composite membrane for DMFC where they produced a Nafion matrix loaded with histidine doped multi walled carbon nanotubes (MWCNTs). Histidine is an imidazole amino acid. In this work, the authors found that the water uptake for the composite membrane was lower than that in Nafion, but the IEC value and the proton conductivity (Figure 4c) was higher in the composite membranes. The authors claimed that this happened due to the nitrogen in the histidine which attracts and attaches to the water present in the membrane via a hydrogen bond, facilitating the proton transport via Grotthuss mechanism (Figure 4d). The membrane proton conductivity displayed an expected drop around 100 °C because the free water escaped easily and only the hydrogen bonded water remained. According to the authors, this is exactly why the regular Nafion displayed higher water uptake (absorbs more free water) but lower proton conductivity (less bonded water). The methanol permeability for the composite membrane was also considerably lower. The low permeability and the high proton conductivity also showed a superior selectivity of the composite membrane in in-situ conditions. This study brought together two different lines of work, CNT based filler and imidazole/ionic liquids (IL) for high temperature membranes. Some more studies on IL based fillers are discussed briefly, later in this section.

Graphene Oxide

As a newly discovered material, graphene has attracted a lot of interest in the last few years and many initial studies looked into polymer-graphene composites for a wide variety of applications. Graphene has also been added and investigated for use in membrane for gas separation. [68] Not surprisingly, graphene used in some initial studies [69, 70] for membranes for fuel cells did not show any promising results. This is because it has high electrical conductivity that would facilitate the electron transport across the membrane decreasing the fuel cell voltage. However, it does offer many other advantages like high mechanical strength, gas impermeability and large surface area. Further investigations diverted the interest of membrane scientists towards the use of graphene oxide (GO). GO is highly oxidized graphene sheet with a carbon to oxygen ratio of approximately 2:1 [71, 72] but unlike graphene, GO is an electronic insulator and a potential filler. The oxidation breaks the π-π bonds, separating the graphene sheets from the graphite stack, and leads to the formation of sp^2 graphitic domains surrounded by disordered sp^3 oxidized domains with oxygen groups. [71, 73] The presence of various oxygen groups (hydroxides, epoxides, carboxyls and carbonyls) turns GO into a very hydrophilic as well as insulating material [74, 75] while still retaining the high mechanical strength and gas impermeability as offered by graphene. GO due to its high surface area, could potentially allow easier proton transport and higher water uptake. [69] It is properties like these (hydrophilicity, electrical insulation and gas impermeability) that have generated a lot of interest in the use of GO as a filler in composite membranes for PEFC and DMFC in recent years.

In an attempt to address the important problem of methanol permeability in DMFC, Choi*, et al.* [76] developed a composite GO/Nafion membrane with the rationale that GO would act as a barrier to fuel because of the higher tortuosity. GO is considered to enhance both

backbone and side chains of Nafion when it is incorporated to the ionic cluster, thus improving both mechanical and thermal properties. The authors claim that the compatibility between both components is guaranteed due to their strong interfacial attraction. This is because just as Nafion presents hydrophobic fluoride backbone and hydrophilic $–SO_3^-$ groups; GO also presents both behaviours, with hydrophobic planes and hydrophilic edges. The authors prepared membranes with GO loading ranging between 0.1 wt.% and 2 wt.%. The authors reported that below 0.1 wt.% the barrier effect of GO to methanol was not observed and above 2 wt.% a homogeneous distribution of GO in the Nafion matrix could not be achieved. Their studies revealed that the permeability for methanol with just 0.5 wt.% of GO was reduced to 60.2% of Nafion 112 at 25 °C. However, the proton conductivity studies revealed an opposite trend showing a decrease with increase in the GO filler content and was reported to be reduced to 55.3% of the pristine Nafion value with 2 wt.% GO loading. This was not completely unexpected as GO alone is not known to be an excellent proton conductor. Consequently, GO membranes were not reported to show high proton conductivity in the initial reports. Later, Chien*, et al.* [77] prepared a composite membrane with sulphonated graphene oxide (SGO)/Nafion for DMFC. The aim of using GO was to reduce the methanol crossover similar to the work reported by Choi *et al.* [76]. However, the addition of polar $– SO_3^-$ molecules bonded in GO was also expected to allow higher proton transport. The authors investigated different amounts of loadings (0.05 to 5 wt.%) of SGO but the ideal ratio was reported to be between 0.05 and 0.5 wt.%. Above this value, it was reported that SGO tends to aggregate. The lowest methanol permeability was reported for membranes with loadings below 0.5 wt.% of SGO, which could achieve 20% lower permeability than commercial Nafion membrane 117 and 115. Moreover, the mechanical resistance (tensile strength) was also reported to be 100% higher than commercial Nafion.

Zarrin*, et al.* [78] functionalized graphene oxide with $-SO_3^-$ groups and prepared a Nafion membrane with sulphonated GO as filler for PEFC. The acids groups were expected to compensate the loss in proton conductivity due to addition of GO, which would reduce fuel permeability. In this study, the authors noticed that the water uptake and IEC for the composite membranes were similar to that of recast Nafion and the composite membrane had a better performance in a real PEFC environment than the recast Nafion. The peak power density for the composite membrane was reported to be more than 3.5 times higher than that recorded with Nafion, and the cell voltage too was higher at all measure currents. Hence, most current studies show that despite the fantastic characteristics of GO, it is necessary to functionalize it with polar groups that can trap water in any situation. Pristine GO which is known to be hydrophilic and has a tendency to trap water molecules in between the graphene oxide sheets via H-bonding. However, as discussed before such kind of water molecules are not able to contribute significantly towards proton conductivity and hence the need to have more sulphonated acid bonded water molecules.

However, while the proton conductivity increases with the degree of sulphonation (DS) in a PEM; its mechanical properties decay, methanol/water permeability increases leading to accelerated membrane deterioration. The introduction of an inorganic group, such as SGO, should help minimize the negative effects of sulphonation of polymers such as loss of mechanical strength since these carbon nanostructures provide increased mechanical strength and also decrease methanol permeability by making the path more tortuous for the liquid fuel. Many studies on functionalised graphene oxide used as filler in different polymer membranes have also been reported in the last few years. Cao*, et al.* [79] developed a composite membrane of GO/poly (ethylene oxide) for use in PEFC. In this work,

GO was modified to have more carboxyl (–COOH) groups in order to increase the proton conductivity. On testing an 80 µm thick membrane with 0.5 wt.% carboxylated GO, the authors found that the membranes displayed excellent mechanical properties such as tensile strength of 52.22 MPa, Young's modulus of 3.21 GPa, and a fracture elongation of about 5%. The GO/poly (ethylene oxide) membrane also showed increased ionic conductivity at 100% humidity as the operating temperature was increased from 25 to 60 °C. This study, however, did not investigate the affect of low RH and performance at temperatures 80 °C or above. Heo*, et al.* [80] reported a composite membrane of sulphonated graphene oxide and sulphonated poly (ether-ether-ketone) SGO-SPEEK for DMFC application with the idea that the sulphonation of GO and SPEEK would increase the number of sulphonic groups and hence provide increased proton conductivity. The authors reported that the sulphonation not only increased the proton conductivity by allowing higher water retention but also improved the mechanical strength and reduced the methanol permeability. Jiang*, et al.* [81] prepared a membrane of sodium dodecyl benzene sulphonate (SDBS) with GO adsorbed on the SPEEK filler to use in DMFCs. SDBS was expected to provide higher ionic conductivity compared to SPEEK, while GO would act as a barrier to methanol along with providing mechanical strength and thermal stability. Their work revealed that the methanol permeability of the membrane SPEEK-SGO/SDBS was decreased by around 50% with 5 wt.% of SDBS when compared to pure PEEK. Considering the positive effect of GO on the selectivity (ratio of proton conductivity and fuel crossover) of the membrane, Lin and Lu [82] investigated the effect of preparation method on the GO/Nafion membranes on its properties and also investigated the performance in a DMFC in the presence of high concentration of methanol. The aim of their work was to compare a dual-layer laminated GO/Nafion membrane, which used a 2D GO paper with a traditional

GO-dispersion based GO/Nafion membrane. This work can be considered as a transitional study, bridging the gap between composites and multilayer membranes. Although the authors did not refer to the membrane as a multilayer, they do call it a dual-layer laminate membrane. The authors first analysed the influence of GO by comparing the performance of GO/poly (vinyl alcohol) (PVA) membrane and pure PVA membranes. The performance of the composite membrane (1.5 wt.% GO) was reported to be better than the pristine PVA membrane because of the reduction of methanol crossover due to the increased tortuosity provided by addition of GO. This was followed by the tests on laminate GO/Nafion and dispersion GO/Nafion membrane. The laminate membrane was prepared using a GO paper hot-pressed on to the Nafion surface, which was expected to improve the interfacial bond between the two layers. Interestingly, the laminate GO/Nafion showed significantly lower water uptake (WU) compared to Nafion 115 (28.8% for Nafion and 10.3% for the laminated GO/Nafion). However, the authors found the laminated GO/Nafion membranes shared this trend with the GO dispersion GO/Nafion and GO dispersion GO/PVA membranes. The improved performance has been previously [83] attributed to the presence of the carboxyl and carbonyl groups in the GO which enable increased ionic conductivity due to the release of protons. In the evaluation of the ion exchange capacity (IEC) values of their membranes, the laminated GO/Nafion membrane showed a slightly greater IEC value. This trend was in agreement with the values observed for dispersion GO/Nafion membranes. The GO/PVA membrane, however, showed a reverse trend and this behaviour remains unexplained. The authors also reported that methanol permeability in the laminate GO/Nafion membranes was significantly lower than that reported in the studies performed by Kumar et al., [83] on GO dispersion based membrane. The decreased methanol crossover was attributed to the orientation of the 2D GO sheets which was previously discussed in the study of Paredes*, et*

al. [84] who proposed that unlike the water molecules, the larger methanol molecules find it difficult to penetrate the GO interlayer spaces. The authors reported that the selectivity in laminated GO/Nafion membrane was 40% higher than that in Nafion 115. Finally, DMFC testing with various high concentrations of methanol revealed that the laminated GO/Nafion membrane demonstrated much higher stability and higher currents even as the methanol concentration increased from 2 M to 6 M. However, beyond this the performance was reported to have deteriorated. On the contrary, Nafion 115 showed a deteriorating performance with increasing methanol concentration as the methanol concentration was increased from 2 M to 8 M.

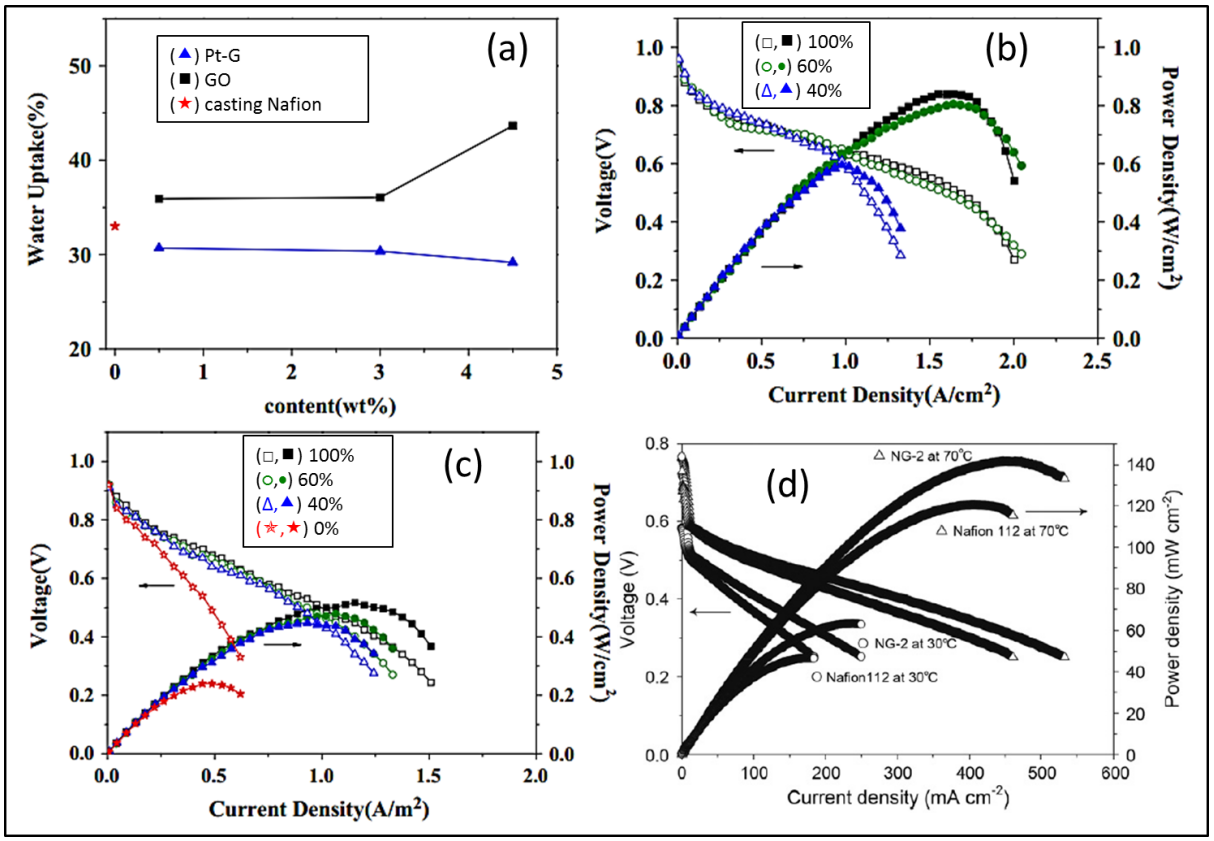

Figure 5: (a) Water uptake and (b) I x V curve for the membrane with 3 wt.% of GO and (c) I x V curve for the membrane with 3 wt.% of Pt-G, changing the humidity from 100 to 40% [85]; (d) The performance of a DMFC with Nafion/2 wt.% GO membrane detailed in Table 1. [76]

More recently, Lee*, et al.* [85] developed Nafion membranes with graphene oxide (Nafion/GO) and with reduced graphene-platinum (Nafion/Pt-G) as fillers to test in PEFC set up. The Pt loading in Pt-G (1.8 nm in average size) was reported to be 38 wt.% and the authors prepared composite membrane loadings with a variable filler content where GO and Pt-G percentage was varied from 0.5 wt.% to 4.5 wt.%. The authors compared the performance of the composite membranes with that of a recast Nafion. The authors reported that all the composite membranes revealed significantly higher tensile strength compared to recast Nafion. However, the water uptake studies revealed that while all GO filler composite showed higher water uptake compared to recast Nafion, all the Pt-G filler composites showed relatively lower water uptake (Figure 5a). The authors attributed the lower WU for Pt-G based composites to the transformation of hydrophilic GO into hydrophobic reduced graphene upon Pt loading and electron loss in GO due to formation of an electrical network resulting from the addition of excess of platinum. Nevertheless, the proton conductivity for Pt-G composites membranes was reported to be higher than Nafion in all the filler content values. The authors claimed that Pt-G being an electronic conductor resulted in higher net ionic conductivity values for the Nafion/Pt-G systems. Interestingly, for the GO filler samples, only a loading of 4.5 wt% GO enabled higher proton conductivity than recast Nafion. The improved performance was attributed to the presence of sufficiently high amount of oxygen functional groups in GO, allowing proton pathways overriding the blocking effect for ionic clusters formed in Nafion by GO. In the PEFC single cell test the 3.0 wt.% Nafion/GO was found to present the best results, (Figure 5c) among all samples, including recast Nafion and was followed by 0.5 wt.% Nafion/GO and 3 wt.% Nafion/Pt-G (Figure 5d for Nafion/Pt-G). The superior performance of GO compared to that of Pt-G was considered to be due to its higher water content and consequently higher

proton conductivity [74]. While the paper was a good attempt to simultaneously investigate the effect of adding GO and Pt-G filler to study the effect on membrane hydration, it did not investigate the effect of variable Pt loading in Pt-G filler on the membrane performance. As the authors attributed the reduced WU of Pt-G systems to excess Pt loading, future studies looking into the performance of such filler with lower Pt content could be useful in improving the performance of such composites and the concept of using metal-rGO systems for self-humidification in membranes. Table 2 summarises the methanol permeability, proton conductivity and selectivity information from some composite membranes and their performance in a FC in comparison with a commercial Nafion. Most of them have a better *in-situ* performance, even if one or other propriety is not as good as that of Nafion.

Table 2: Characteristics of composite membranes for PEFC/DMFC compared with Nafion membranes. Where selectivity is defined as proton conductivity divided by methanol permeability.

Study	**Membrane**	**FC Type**	**Permeability to methanol ($cm^2\ s^{-1}$)**	**Proton conductivity ($S\ cm^{-1}$)**	**Selectivity ($s\ cm^{-3}$)**	**Performance in a single FC**
[76]	GO (2 wt.%) /Nafion	DMFC	↑ (~$4e^{-7}$)	≈ (~0.02)	↑ (5.05 x 10^4)	↑
[60]	ZTP(10 wt.%) /SPEEK	DMFC	↓ (~$1x\ 10^6$)	≈ (~0.06)	↑(65 x 10^{-3})	NA
[86]	SGO/Nafion	DMFC	35% ↓	↑	NA	↑ at 60 °C
[78]	SGO (10 wt.%)/Nafion	PEFC	NA	≈ (~10^{-1})	NA	↑
[47]	SiO_2/Nafion	PEFC	NA		NA	↑ in low RH

[59]	TiO_2/Nafion	PEFC	NA	↑ (~0.3)	NA	↑
[61]	$SZrO_2$/Nafion	PEFC	NA	NA	NA	≈
[138]	Pt-G/ SiO_2/Nafion	PEFC	NA	↑ (~0.093-3 wt.% Pt-G/3 wt.% SiO_2)	NA	Best with 1.5 wt% Pt-G and 3 wt.% SiO_2
[139]	ZrNT (nantotubes) /Nafion	PEFC	NA	↑ (0.140 at 80 °C)	NA	↑ in low RH and at 80 °C
[140]	f-MWNT /Lotek 4200	DMFC	↓ less than $0.5x10^6$	↑ (~0.025)	NA	NA

*↑ higher with respect to Nafion; ↓ lower with respect to Nafion; ≈ approximate the same; NA = Not applicable

In general, the complexity of composite membrane has increased in the recent past. There are a number of studies reported on composite inorganic and organic materials, especially where organic fillers are modified with inorganic particles such as PTFE-SiO_2 [87, 88]. The advantage in using this kind of system is that the good interaction between the organic filler and the polymeric matrix is still present. Such complex structures however, require that the composite materials and fillers be properly characterized before being tested in a membrane structure. Many of the studies on GO fillers often do not provide detailed material characterization information of the GO used. GO is a highly heterogeneous material, factors like degree of oxidation and C:O ratio in the GO or SGO are often not

investigated or reported which makes comparison of various studies using variable types of GO is therefore very difficult. Often the mode of oxidation for GO preparation or reduction for reduced graphene when using Pt-G fillers have a significant impact on the ratio of residual oxygen species which would have variable effect on the behaviour of the GO /G-Pt filler. These could be some of the factors responsible for inconsistent and contradictory reports on the effect of GO filler in composite membranes. There remains the need for more systematic and thorough experimental studies in order to clearly identify the role and behaviour of GO and GO based fillers, especially where proton conductivity is concerned.

Other Composites

Besides the studies on carbon nanostructures and metal oxides as loading/filler in composite membranes, there are new and different approaches using ionic liquids and composite membranes as mentioned before. [67] Padilha*, et al.* [89] claims that with ionic liquid added to the electrolyte, the efficiency of the PEFC can be increased over the usual 40% to 61%. Xu*, et al.* [90] functionalized the graphite oxide with 3-aminopropyltriethoxysilane ionic liquid to use as a filler in the membrane with polybenzimidazole (PBI) matrix to use in IT and HT-PEFC. Ionic liquids are liquids with ions (salts), which would bond with the GO and could facilitate the hopping mechanism. The proton conduction in ionic liquids therefore is not water dependent. In this particular work, the authors used phosphoric acid with the PBI membrane, because it provides higher conductivity. While phosphoric acid can damage the membrane if used in excess, by using ionic liquid fillers, the membrane did not need high amounts of phosphoric acid to obtain high proton conductivity. Lee*, et al.* [91] also developed a composite membrane with ionic liquid to use in PEFC with no humidification. The matrix was sulphonated poly(imide) and

the ionic liquid was diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]). In this work, the authors proved that the proton conductivity of the composite membrane is higher (approximately 10^3 times at 160 °C) than that of sulphonated poly(imide) alone. However, the single cell test was just conducted at ~80 °C. A similar idea of composite membrane was also developed by Malik*, et al.* [92], their matrix consisted of cross-linked SPEEK and the ionic liquid 1-buthyl-3-methyl-imidazolium trifluoromethanesulfonate ([bmim][TfO]). They found that the SPEEK had little influence on the proton conductivity. As the amount of [bmim][TfO] was increased, the ionic conductivity also increased and seemed independent of temperature. The authors concluded that the ionic liquid provides ionic mobility and flexibility to the membrane. Similar to Lee *et al.*, [91], Liu*, et al.* [93] made a composite membrane with PBI/[dema][TfO], but it was used in a H_2/Cl_2 fuel cell and not the H_2/O_2. To use this FC the membrane has to work in low or zero water environment, as otherwise the hydrogen chloride (reaction product) will consume all the water. In this case, the membrane showed good results for the fuel cell. The conductivity was reported to increase with the increase in the amount of ionic liquid.

All these reports used ionic liquid based membranes for fuel cell to operate in low humidity conditions. Ionic liquids seem to be a good alternative to traditional filler materials in composite membranes. The considerably larger number of free ions allows easier pathway for protons as the distance between the neighboring active sites is shorter and the protons can move freely. Another possible line for future studies is to incorporate use of ionic liquids in multilayer membranes (multilayer membranes are discussed in the next section). This is because phosphoric acid is widely used in multilayer membranes and the use of ionic liquid would help decrease the amount of acid used in the membrane, minimizing the damage to

the fuel cell due to the aggressive conditions generated in the presence of the acid. Further detailed discussion on ionic liquid based membranes is beyond the scope of this review. However, the authors recommend other reviews by Buzzeo*, et al.* [94] and Armand*, et al.* [95] on this subject for extensive discussions.

3. Multilayer membranes

Composite membranes and alternatively sulphonated polymers have been widely studied to substitute Nafion membranes. Nevertheless, there is a strong concern regarding the solubility of sulphonated polymers in water, and a consequent drop in the water dependent proton conductivity. An approach adopted recently to minimise these effects is the use of multilayer membranes. This approach is expected to help keep the best proprieties of each layer/component intact while overcoming the drawbacks of each by using and combining layers of different membranes/polymer materials.

The concept of multilayer membranes, although new to fuel cells, is not new to membranes in general. In the past, multilayered polyelectrolyte membranes have been developed extensively for applications other than fuel cells such as filtration systems (air and gases purification), dialysis, ionic filtration membranes, etc. which required ion permeability through the electrolyte. Among these applications, multilayer polymer electrolyte membranes are probably most extensively researched in the field of dialysis. For example, Shan*, et al.* [96] used multilayered system for nano-filtration applications where they observed the selectivity for $MgSO_4$ ions. Hong*, et al.* [97] worked with a system of sulphonated polystyrene and poly(diallyldimethylammonium chloride) for ionic separation

using nano-filtartion. Sheng*, et al.* [98] using layer-by-layer (LbL) method developed a poly[(N,N'-dicarboxymethyl) allylamine] and protonated poly(allylamine) multilayer membrane to use as ion separator, providing higher Cu^{2+} ion permeability compared to Mg^{2+} ion. Some other studies [99-102] worked on multilayer polyelectrolytes for ion selectivity, investigating the effect of a) changing the layers and, b) the method of multilayer formation or even the ions transport. Although these systems differ in many aspects from PEFC membranes, the main idea of ion permeability through a multilayer membrane is common to all. Table 6 below summarises the advantages and disadvantages of composite and multilayer approaches.

Table 6: Comparison of composite and multilayer approach for membrane preparation and new trends in these.

Approach/Method	Composite Membranes	Multilayer Membranes
Advantages	Fast manufacture Known physical and chemical proprieties calculations	Countless combination of materials and layers Keep the characteristics of each layer intact
Disadvantages	Difficult homogeneity Polymer matrix must be resistant to water	Extra interface problematic Longer time manufacture
New trend	Use of carbon nanostructures and ionic liquids	Inner layer not just as a polymer, but with complex formulation

In the last 4 to 5 years, interest has slowly developed in the use of multilayer membranes for PEFC/IT-PEFC and DMFC applications. The most important function for PEFC membranes

is the transportation of H^+ ion. While H^+ is a small ion, it still has the same characteristics and behaves as any other cation. As such, the rules of transport in multilayer membranes for nanofiltatrion can be carefully applied in these low temperature fuel cells. Hence, the experience and literature available on membrane development is, therefore, expected to enable not only a more professional approach towards the IT-PEFC and DMFC multilayer membrane development but also minimise the glitches and errors in the various preparation and layering procedures adopted for achieving the desired end. This section discusses multilayer membranes used for FCs in the last few years. Unlike the composite membranes where the division was made on the basis of the nature of the materials, the multilayer membranes in this section are divided according to routes of preparation. This is because multilayer systems are more complex and may often involve many different types of materials constituting the various layers of the same membrane. As such, here we classified multilayer membranes on the basis of preparation methods. There are 3 main categories that the multilayer membranes can be divided into based on preparation methods are: i) Hot pressed, ii) Solution cast and iii) Dip coated. There are some novel approaches which do not fit into any of the three widely used categories and these are briefly discussed towards at the end of this section.

3.1. Hot Pressing

Hot Pressing is the simplest route to produce a multilayer membrane. Simply put, the process just involves pressing of two or more independent membrane layers (that are already cast) at high temperature. The membranes used for hot pressing can be commercial extruded membranes or those solution cast in the lab. When the layers are heated (usually close to or slightly below the polymer's glass transition temperature, *Tg*) under high pressure, they stick together via a mechanical bond between them to form a multilayer

membrane. Yang and Manthiram [103] fabricated a multilayer membrane with two external layers of Nafion membrane and one internal layer of SPEEK membrane by hot pressing to use in a DMFC. For control studies, this was compared with a single recast Nafion membrane of thickness similar to that of the multilayer membrane and another membrane consisting of three layers of Nafion combined by hot pressing. This was one of the first studies with multilayer membranes for fuel cells. It was an important study, not only because it was a first from the fuel cell point of view but also because it was carefully planned a) to compare performance with a single membrane which had the same thickness as the multilayer and b) to take into account the possible effect of inter-layer interaction on the membrane performance by using the three layers of Nafion membrane hot-pressed as one for the control study. Many studies have since then been reported on hot pressed multilayer membranes for fuel cell applications. Based on the understanding that the strongly sulphonated polymers which are targeted to achieve higher proton conductivity invariably suffer from the drawback of increased water solubility, Chen*, et al.* [104] prepared a layered Nafion membrane with an inner layer of sulphonated polysulfone (SPSU) with a 87% degree of sulphonation (DS). As SPSU can be dissolved in water, SPSU was placed between two layers of Nafion (with the electrode) and the three layers were hot pressed together to block the excess amount of water that could wash out SPSU. With 87% degree of sulphonation (DS), SPSU alone was reported to have three times higher water uptake than Nafion, and more than 50 times higher water uptake at 127 °C than at 20 °C. The only drawback, as discussed, is that such an SPSU membrane dissolves in water at 80 °C due to the higher $–SO_3^-$ content per repetitive unit of polysulphone as these polar groups have strong affinity for water. However, as expected, when the layered membrane Nafion/SPSU/Nafion was used in a PEFC system, SPSU was not washed or dissolved and

demonstrated a stable performance during the FC operation at 120 °C. In another fascinating study, Peng*, et al.* [105] developed a study looking into the water management in a multilayer membrane. The membrane was made by hot pressing of two commercial membranes: Nafion NRE212 and Aquivion^{TM} E79-05s, each having a thickness of 50 µm. The hot-pressing in this method was performed in two steps: i) pressure of 0.05 MPa, at 170 °C was applied for 150 s; ii) pressure of 3.5 MPa at 170 °C was applied for 210 s. The authors claimed that at this temperature the layers do not delaminate. The adhesion test of the membranes was carried out via a series of successive hydration and dehydration cycles performed at 80 °C. The water content and distribution were evaluated by in-situ Raman micro-spectroscopy, during fuel cell operation. These are novel methods of testing layer adhesion and water content compared to methods used in most reported works which use tensile testing and water uptake measurements for testing these two parameters, respectively. According to the authors, the use of in-situ Raman micro-spectroscopy enabled the measurement of the actual hydration in the membrane in the region swept by the hydrated feed gas and allowed real-time monitoring of the water concentration evaluation under the changing working conditions inside the cell. Figures 6a and 6b show the water concentration profile in the MEA at a current of 222 mA cm^{-1}. The graphs further show that in both the cases water content was not lost at the interface suggesting that the method developed to press the two membranes was efficient and formed a continuous interface. This work may lead to more comprehensive studies on water management in multilayer membranes. The concept of interface is a new parameter to be studied in the FC membrane development and many proprieties, such as water behaviour and proton transfer are still not understood, for multilayer membrane systems. A wide range of studies would be required on both commercial as well as lab-scale membranes which are prepared using a

variety of materials in order to develop a proper understanding of how the different layers behave and interact with each other at the interface before the characteristics and properties of the multilayer membranes interfaces can be fully appreciated.

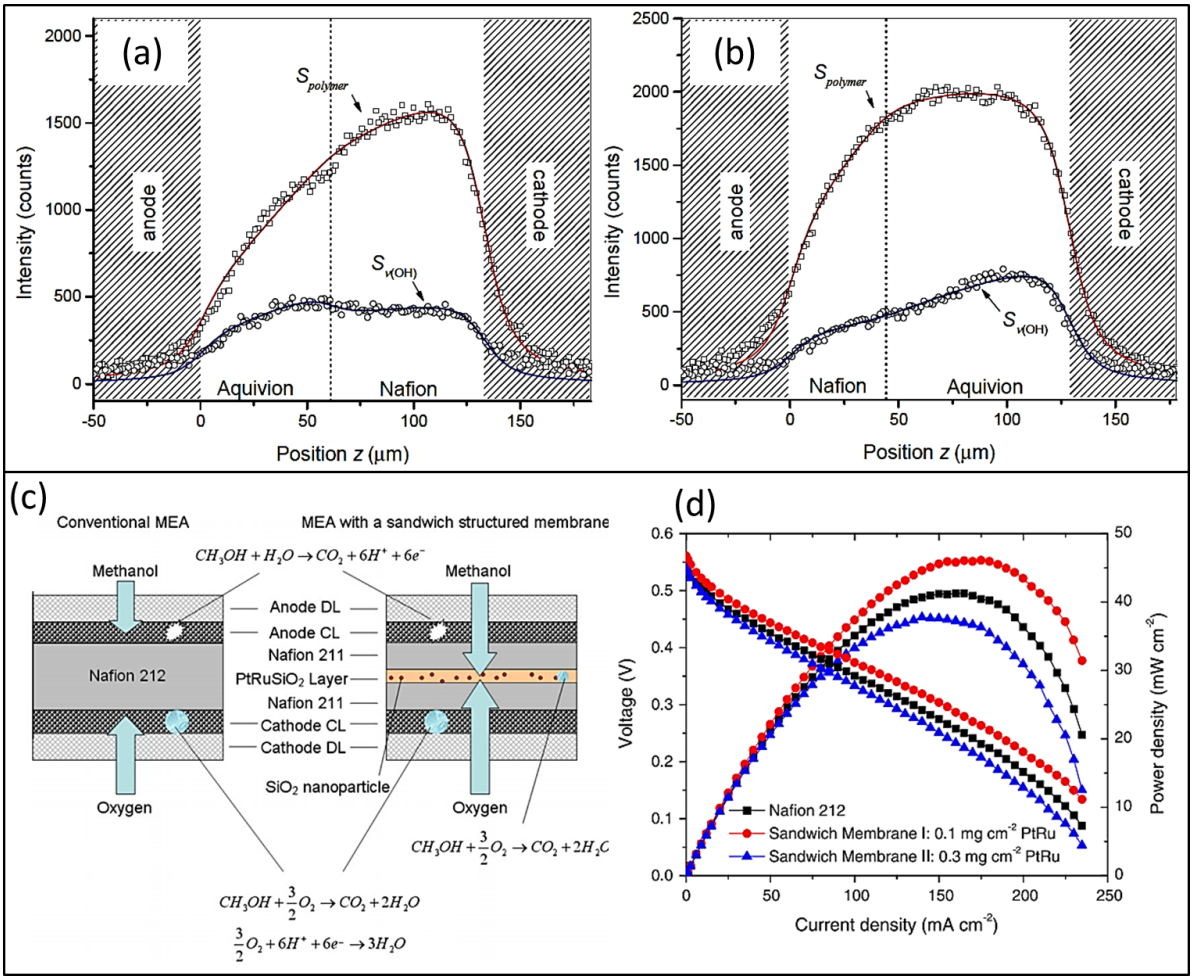

Figure 6: (a-b) Water concentration profile in the membranes: a) Aquivion/Nafion and b) Nafion/Aquivion. [105] (c) Schematic of multilayer membrane structure as shown by Wu et al. (d) DMFC single test with the multilayer membranes. [106]

Just like composite membranes, multilayer membrane structures in a fuel cell can also be prepared by combining materials other than polymers. Wu, *et al.* [106] developed a very interesting membrane for DMFC system. This multilayer structure contained three layers that were hot pressed together, where the two external layers were of Nafion 211 and the

inner was a “reaction” layer as shown in Figure 6c. This reaction layer was made of PtRu and SiO_2 nanoparticles dispersed in Nafion. The main idea behind such an arrangement was that any methanol and oxygen that would manage to permeate the outer membrane react with the inner reaction layer. The water generated in the middle of the structure in this way would help maintain the membrane humidification while reducing the membrane’s internal resistance and improving the proton transport. When the membrane was tested in a single cell DMFC and its performance compared with that of a single layer of Nafion 212 (both 50 µm of thick), the multilayer membrane showed better performance (Figure 6d). The authors claimed that the reason for the improved performance was the improved water management within the membrane due to the presence of the PtRu and SiO_2 in the reaction layer.

GO based multilayer membranes, due to the materials interesting characteristics, have also been evaluated in various studies for using in fuel cells. Gao*, et al.* [107] prepared films of GO and ozonated GO by commonly used filtration method. These films were then hot pressed between Nafion layers. The authors claimed that after some tests the ozonated GO showed better results in a PEFC. However, those tests were evaluated only at low temperature (35 °C) and so the study did not report on the absorption of water and performance under more aggressive conditions.

3.2. Solution Casting

Casting is the first and the oldest method used for the preparation of polymer membranes and films. Together with hot-pressing, casting is also a widely popular method for multilayer membrane preparation. In fact the two processes are commonly combined for multilayer membrane preparation as hot pressing cannot be carried out unless cast membranes are

available for the same. The process of solution casting includes the preparation of a polymer solution in a suitable solvent, which is then poured into a flat surface style vessel. The vessel is then usually placed in an oven to evaporate the solvents and the membrane is formed at the bottom of the vessel. After the first layer is ready, the second polymer solution is poured over the first layer and is dried in a similar way. In this process, a chemical bond is formed between the layers. The process can be used to prepare as many layers as required with virtually any combination of polymers.

Although the concept of a layered membrane with a sulphonated polymer has not been exploited much in the field of PEFCs, their use in DMFC have achieved some success [108-111]. Luo*, et al.* [112] developed a layered PEM of Nafion/SPEEK to use in a vanadium redox flow battery. The presence of an inner layer of a non-fluorinated polymer (SPEEK) reduces cost and increase proton conductivity. As discussed earlier, usually these polymers do not possess a high chemical stability, so Nafion or another PFSA membrane would help provide chemical stability and minimise degradation rate for the overall structure. Unlike the work reported by Chen *et al.,*[104] in which membrane was made by hot pressing the layers together, Luo *et al.*, [112] and co-workers prepared this membrane by casting. The authors claimed that in this way the possibility of delamination of membrane layers, which decreases the battery performance, is minimised since the layers are bonded chemically and not just mechanically. The authors cast SPEEK in a flat glass, which was then dried and Nafion were cast over the SPEEK membrane, leading to a gradual interface between the layers. This study by Zhang et al revealed that in the case of a vanadium battery the transport of ion (VO^{+2}) was lower in the Nafion/SPEEK membrane than in recast Nafion. The authors attributed this to the structure of SPEEK. However, the IEC values for Nafion/SPEEK

membrane were considerably higher. Marrony*, et al.* [113] also developed a bilayer membrane with SPEEK/Nafion by recast method investigating the different degrees of sulphonation of SPEEK for application in PEFC. The authors reported that no evidence of any tendency towards delamination was observed even under prolonged fuel cell operation of over 900 hours at 110 °C. Another interesting observation reported in their study was that different polymer multilayer systems even with sulphonated polymer of similar chemical composition can show different water uptake characteristics which can influence the direction of water production at the anode or cathode in an operating fuel cell. In another study, Yang *et al.* [111] took a slightly different approach and prepared a cast multilayer membrane which was prepared with five thin layers of sulphonated poly(ether ether ketone) (SPEEK) and poly(vinyl alcohol) (PVA) placed alternately. The authors observed that the tendency of PVA to swell was restrained by the presence of alternately arranged SPEEK layers. Although the WU was low, the multilayer membrane achieved a good performance in DMFC because of its high selectivity, which meant that the methanol crossover was almost alleviated. Li*, et al.* [114] developed a three layer membrane, where the two external layers were made of sulphonated poly(imide) (SPI) and the inner layer was a SPEEK-SPI blend with 10 to 40 wt.% of SPI. The authors compared the multilayer membrane with a single membrane of SPEEK-SPI blend (10 to 40 wt.% SPEEK). The SPI membrane was solution cast, then the SPEEK membrane was cast over it, which was followed by another SPI layer. The SEM analysis revealed that the two external structures are similar while the inner layer was thinner and different. The authors suggested that the inner layer was thinner because the SPEEK migrated to the external layers. The little difference in the external layer thickness may also be caused by the migration of SPEEK, since the SPEEK just dries over one side. The authors found that SPEEK alone had higher water uptake than all others and the

blend membranes displayed higher WU than the equivalent multilayer. The authors also reported that the proton conductivity of some of the triple-layer membranes was found to be higher than that of the corresponding blend membranes. This work put forth a balanced view of multilayer and composite/blend membranes suggesting that not all multilayer membranes work better than composites. The study revealed that the choice of the polymer and the method of preparation play a significant role in determining the performance of the membrane. In this case, the composite membrane was a better choice and also simpler to produce.

In the past 2-3 years, a wide variety of structures including variable number of layers, combination of organic and inorganic membrane layers have been investigated and reported for multilayer membranes using casting [115, 116]. Padmavathi*, et al.* [117] developed a multilayer membrane by casting, where the inner layer consisted of SiO_2 mixed with 5wt.% aminated poly(sulphone) (APSu) sandwiched between two external layers made of sulphonate poly(sulphone) (SPSu). The APSu was used in order to retain water in the matrix and it was also expected to lower methanol crossover. The authors tested the membranes in both DMFC and PEFC systems. The authors studied five different multilayer structures where the amount of SiO_2 was varied between 2 and 10 wt.% and the total thickness was maintained around 120 µm. The authors found that in the PEFC the single SPSu displayed higher power and voltage (Figure 7a and b), while in DMFC the performance of the multilayer with 2 wt.% SiO_2 was found to be the best and attributed this to the higher selectivity of the multilayer. The superior performance and durability in DMFC is due to the very low methanol permeability. This is because the layer of SiO_2 and APSu offers more tortuosity to the path available for methanol molecule to permeate through the membrane

compared to the conventional composite membrane. This study highlighted the viability of multilayer membranes when comparing the DMFC and PEFC systems. While some multilayers maybe suitable for DMFC they may not be as suitable for PEFC. There is still a high demand for more robust and highly selective membranes for DMFC environment but the same membrane may not necessarily bring a significant benefit to PEFC system. It would, however, be interesting to see how such a membrane would behave in an IT-PEFC environment where water retention is a very critical parameter.

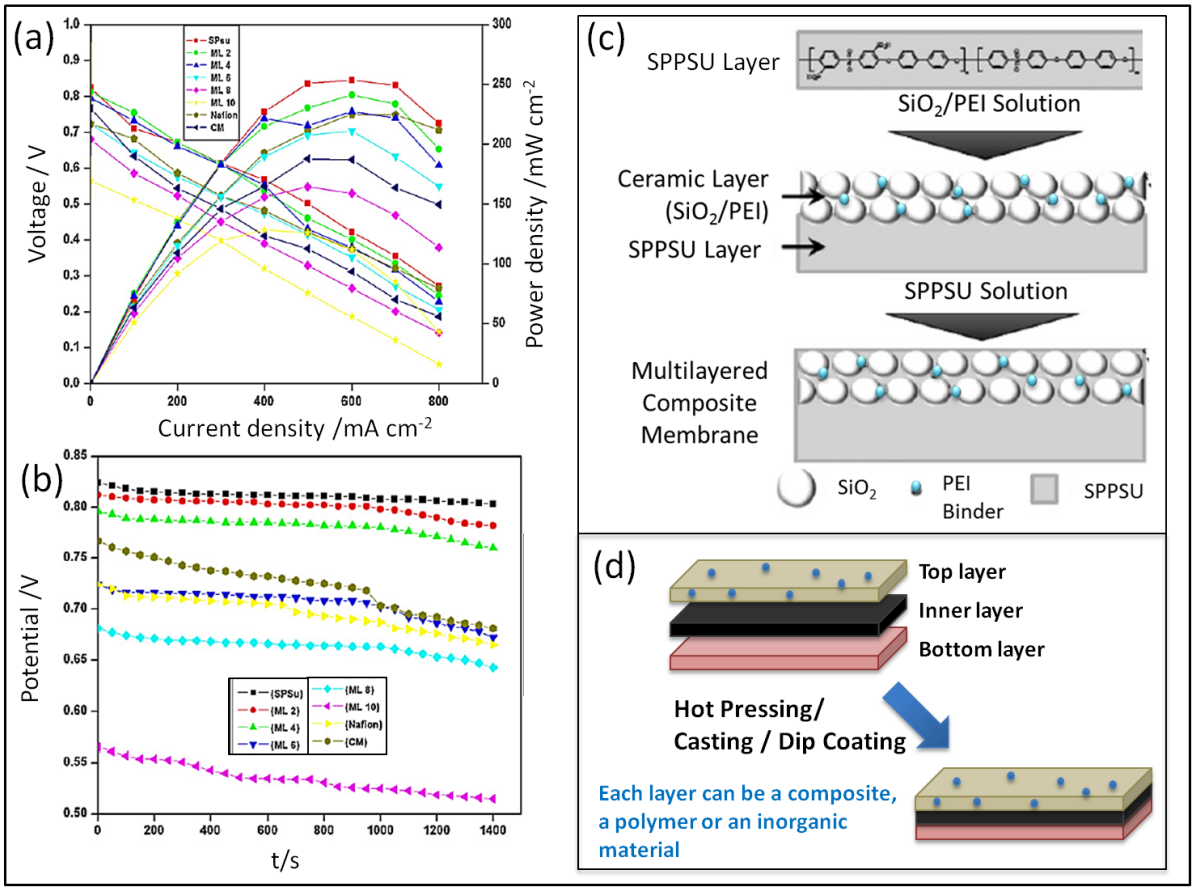

Figure 7: (a) Single PEFC cell test; (b) PEFC durability test. [117] (c) Schematic of the multilayer membrane with SPPSU external layers and inner layer of SiO_2 + PEI (d) Schematic showing the basic concept of a multilayer membrane

The main idea in PEMs is to find an optimum behaviour between excellent proton transport and maximum resistance to fuel crossover. If the path is too tortuous, then neither the proton nor the fuel would pass through the membrane. If the path is completely non-tortuous both proton and fuel would crossover to the cathode side. Consequently, studies have been looking into identifying the best possible middle-path. The inferior results for multilayer and composite membranes with inorganic filler materials at high RH just show that in these conditions there is no need of inorganic fillers to transport the protons. But when used under low RH conditions the hygroscopic silica helps retain the water. Lee *et al.* [115] prepared a multilayer membrane with an inner layer of SiO_2 via solution casting. This was aptly termed as a 'multilayer-structured composite membrane' by the authors. The two external layers in this multilayer were cast of sulphonated poly(phenyl sulphone) (SPPSU). The inner layer, however, was a composite of SiO_2 and amorphous thermoplastic polyetherimide (PEI) binder (Figure 7c). The authors claimed that such an arrangement of SiO_2 would provide an independent ceramic layer comprising close-packed SiO_2 nanoparticles in contrast to a bulk composite membrane which would consist of randomly dispersed SiO_2 nanoparticles. Further testing and characterisation of the membranes by the authors under low (RH of 10%) and high (RH at 100%) humidity conditions (Table 3) revealed that this arrangement of SiO_2 was not only effective in suppressing dimensional change in SPPSU but also in enhancing proton conductivity of the multilayer composite membrane. The authors also reported that the decrease of proton conductivity in low humidity conditions, which is commonly encountered in conventional water-swollen membranes, was minimised in these multilayer composite membranes.

Table 3: Proton conductivity at 100% RH as a function of the temperature and at 10% RH as a function of time [117].

	Temperature (°C)	Proton conductivity (S cm^{-1})	Time (min)	Proton conductivity (S cm^{-1})
Pristine SPPSU	30	~ 0.115	0	~ 0.090
	40	~ 0.123	30	~ 0.067
	50	~ 0.135	60	~ 0.015
	60	~ 0.156	90	~ 0.01
	70	~ 0.172	120	~ 0.00
	80	~ 0.217	150	~ 0.00
Bulk Composite	30	0.065	0	~ 0.053
	40	~ 0.078	30	~ 0.051
	50	~ 0.086	60	~ 0.041
	60	~ 0.094	90	~ 0.025
	70	~ 0.106	120	~ 0.023
	80	0.118	150	~ 0.000
Multilayered Composite	30	0.075	0	~ 0.056
	40	~ 0.086	30	~ 0.055
	50	~ 0.100	60	~ 0.048
	60	~0.108	90	~ 0.037
	70	~ 0.124	120	~ 0.027
	80	0.137	150	~ 0.008

Table 4 displays a compilation of the proton conductivity and water uptake values reported for various multilayer membranes prepared via hot-pressing and solution casting. There are more studies reported for use of multilayer membranes in DMFC than for PEFC. Although some of the reported works investigated membranes with thickness lower than 100 μm, most of the reported works used sulphonated polymers in one or all layers combined with mechanically strong polymers such as SPEEK.

Table 4: Proprieties of hot pressed and solution cast membranes.

Study (Ref no.)	**FC**	**Layers**	**Route**	**Thickness (μm)**	**σ (S cm^{-1})**	**WU (%)**
[118]	DMFC	Chitosan/N/Chitosan	C	100	0.1635 – at 90 °C	NA
[111]	DMFC	1 or 5 bilayers: SPEEK + PVA	C	NA	for 1 bilayer: 0.017; for 5 bilayers: 0.055 at 80 °C	1 bil - 76.2; 5 bil - 30.5
[108]	DMFC	SPEEK/SPDS-diph/SPEEK	C	5--30	0.031 at 80 °C	18.2
[103]	DMFC	N/SPEEK/N	HP	115-135	NA	NA
[114]	DMFC	SPI/SPEEK/SPI	C	NA	0.149 at 100 °C	31.48
[115]	PEFC	SPPS/SiO_2 + PEI/ SPPS	C	120	0.137 at 80 °C	NA
[119]	PEFC	SPSU/PTFE	HP	40	0.00256	NA

*C = cast; HP = hot pressing; N = Nafion; SPEEK = sulphonated poly(ether ether ketone); PVA = poly(alcohol vinyl); SPDS-diph = sulphonated poly(diphenylsulfone - diphenol); SPPS = Sulphonated poly(phenyl sulphone); PEI = polyehterimide; SPSU = sulphonated poly(sulphone); SPI = sulphonated poly(imide); NA = not applicable.

3.3. Dip Coating

Another common route for producing membranes is dip coating. This method is capable of producing the thinnest membranes, but it is also the one with more limitations associated with it. The method involves producing an initial membrane (or using a commercial membrane) using any of the two methods listed above. Then, a solution of the polymer that will form the external/next membrane layer is made in an appropriate solvent. The initial

membrane is then dipped in the polymer solution and the polymer solution gets attached in both sides of the initial membrane. The resultant three-layer membrane is then allowed to dry. Once the membrane is dry, this process of dipping can be repeated as many times using another (or same) polymer solution depending on the polymer needed and the number of layers required. One of the major advantages of this method is that this process allows the formation of multilayer membranes with large number of thin layers such that the final thickness can still be 15-20 µm even when using 10-20 layers. Wang*, et al.* [120] developed a multilayer membrane using this process where the inner membrane was a sulphonated polyimide (SPImd) which was then dipped in a Nafion solution. The authors suggested that the Nafion would adhere to both sides of polyimide providing a higher durability to the central layer. With this method, the authors achieved an extremely thin composite membrane of 15 µm, with each Nafion side layer of 2 µm thickness. Lin*, et al.* [121] also prepared a multilayer membrane with Nafion-SPimd-Nafion. Here, sulphonated poly(amic acid) (SPAA) was used as a precursor. After the coating, the membrane was dried and SPAA imidized to SPImd. The authors carried out the imidization as the last step during solvent evaporation. According to the authors, this helped improve the interaction between the Nafion and SPImd layers. The in-situ PEFC performance of the multilayer membrane was compared to that of SPImd alone membrane and the multilayer showed a better performance. The authors attributed the enhanced stability to the use of Nafion layers and found that the performance of the multilayer was similar to that of commercial Nafion 212 at 70 °C. Zhong*, et al.* [122] achieved lower methanol crossover and better selectivity (in DMFC) with a multilayer membrane made with the Layer-by-Layer (LbL) method which is similar to dip coating. The authors prepared the base layer of silicon containing sulphonated polystyrene/acrylate (SisPS/A) which was dipped alternately in solutions of chitosan and

SisPS/A making the total number of these bilayers between 5, 10 and 15. The membrane was then heated to achieve a crosslinked structure in order to enhance the mechanical strength and durability. The authors found that the durability of the polymer coated by cross-linked structure helped reduce the methanol permeability by facilitating higher selectivity (relation between fuel crossover and proton conductivity). However, the authors also reported that the crosslinking resulted in suppression of some hydrophilic sites. As a result the water uptake of the multilayer membranes was reported to decrease with the increasing number of cross-linked LbL self-assembled bilayers. The authors reported that the water uptake of SisPS/A membrane was reduced from approximately 50.1% at 25 °C, to 47.2%, 46.6% and 45.7%, for the the c-SisPS/A-CS membranes sandwiched between 5, 10 and 15 bilayers, respectively. Consequently, the water uptake of the multilayer membranes was reduced and the resultant proton conductivity of these multilayer membranes was found to be lower than that of Nafion. However, in the absence of any in-situ testing in this study, the overall effect of increased selectivity and reduced proton conductivity remains debatable especially since some other studies on DMFC systems, as mentioned earlier, seem to show improved/ enhanced performance simply due to reduced methanol crossover. Yuan*, et al.* [123] also attempted to reduce the methanol permeability in DMFC by developing a multilayer membrane via dip coating method. In this study, the authors immersed Nafion in poly(diallydimethylammonium chloride) (PDDA) and graphene oxide solution in succession. The Nafion membrane (due to the sulphonic groups on the surface) and the GO (due to the carboxyl and the phenolic hydroxyl groups) are both negatively charged while PDDA has a positive surface charge. Thus, just due to the difference of charges all layers were held together (Figure 8a). To evaluate the methanol crossover, the authors compared the prepared multilayer membrane with Nafion membrane (Figure 8b)

and concluded that the multilayer presented lower methanol oxidation current at the same voltages, confirming that the methanol was being blocked better in the multilayer system. All the multilayer membranes show superior performance compared to Nafion (figure 8c), but the performance decreased as the number of bilayers increased. The authors discussed that the better performance compared to Nafion was achieved because the bilayers blocked the methanol. However, as the number of bilayers increases it may also make the proton transport difficult. Hence, in order to achieve the optimum performance, the number of layers and thickness of each needs to be carefully examined for each polymer/multilayer system.

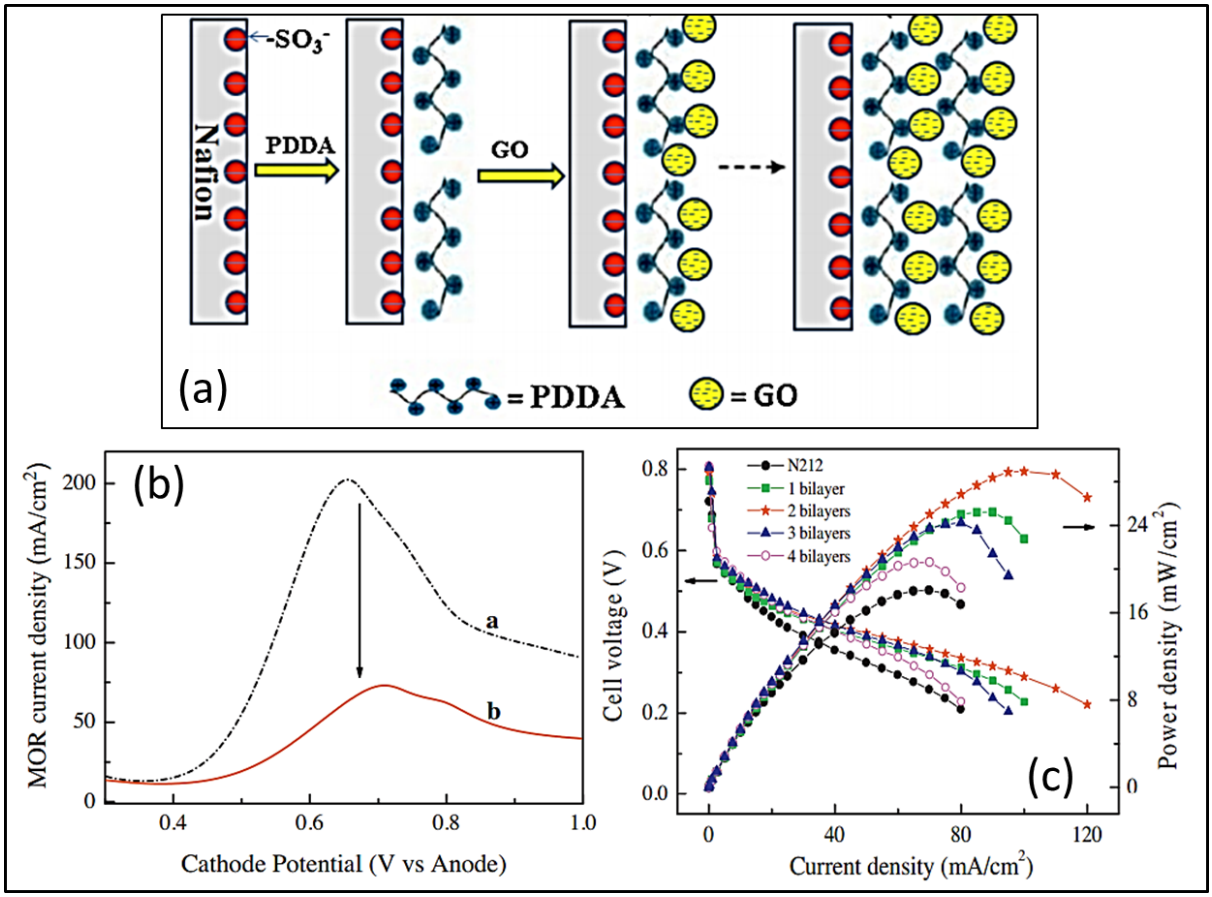

Figure 8: (a) Schematic of the Nafion, PDDA, GO multilayer membrane; (b) methanol crossover test for a) Nafion and b) 2 bilayer membrane; (c) DMFC single test studies for various bilayers. [123]

Table 5 shows the water uptake and proton conductivity values reported for multilayer membranes prepared by dip coating. In these methods the number of layers usually is much higher than those prepared using solution casting and hot pressing (3- 5 layers) methods. The proton conductivity changes considerably due to the number of layers, the layer thickness and also the material of the polymers or composite materials used. Some of them show higher values than those of Nafion under the same conditions. The dependence on the material is evident; even when the method is suitable for the application, if the material is not fit for FC, the results will not be satisfactory. The same trend can be seen for water uptake, although the water uptake values for the multilayer with a highly sulphonated polymer inner layer are usually reported to be lower when compared to the equivalent monolayer of the sulphonated polymer alone. More important than water uptake, are the dimensional variations in polymer layers. In multilayer structures the external layers block these variations, especially in dip coating due to the great number of layers.

Table 5: Properties of reported multilayers prepared by dip coating

Study	FC	Layers	No. of layers	σ (S cm^{-1})	WU (%)
[120]	PEFC	N/SPI/N	3	0.07 (at 80 °C)	NA
[124]	PEFC	SPFEK + PDDA/PSS	NA	0.061 (at 80 °C, 100% RH)	47 (at 30 °C)
[125]	DMFC	N + ScPAESu/GLU	1 (initial) + 1 to 50x 2 (dip both sides)	0.067 (Layers: 25 x2, at 30°C)	21.3
[126]	DMFC	SPAEK + PAni	1 + 5 x2	0.24 (at 80 °C)	93.8
[127]	DMFC	N + PAH/PSS +salt	1 + 5 up to 20 x2	0.08791 (Layers: 5 x2, in 0.1M NaCl at 22°C)	NA
[128]	DMFC	N + HPT/PDDA	1 + 1 up to 5 x2	0.03 (Layers: 5 x2)	NA
[129]	DMFC	PE/PSS + PVI/PAAmHS	1+ 1 x2	0.122	NA

[130]	DMFC	SPAEK + PWA/PPy	1+ 1 to 5 x2	0.0299 (Layers: 10x 2, at 80°C)	49.85
[131]	DMFC	N + SPAEK-c/Chitosan	NA	0.131 (At 80°C)	23.5
[109]	DMFC	N + PDDA-PAA	NA	0.086	NA
[109]	DMFC	PAH-PAA	NA	0.068	NA
[132]	DMFC	PPy/N/PPy	3	NA	NA

*SPS = sulphonated polystyrene; D = dip coating; N = Nafion; ScPAESu = sulphonated cardo poly(arylene ether sulphone); GLU = glutaraldehyde; SPAEK = sulphonated poly(aryelene ether ketone); PAni= polyaniline; PAH = poly(allylamine hydrochloride); PWA = phospotungstic acid; PDDA = poly(diallyl dimethyl ammonium chloride); SPI = sulphonated polyimide; PE = poly(ethylene); PSS = poly(styrene sulfonic acid); PVI = poly(vynilimidazole); PAAmHS = poly(acrylamide methyl propane sulfonic acid); PPy= polypyrrol; SPAEK-c = sulfonated poly(arylene ether ketone) bearing carboxyl groups; PAA = poly(acrylic acid); WU = water uptake; SPFEK = sulfonated poly(fluorenyl ether ketone), PAN = poly(acrylonitrile). All the WU are at room temperature if not informed.

Apart from the preparation methods discussed above many other novel routes have also been developed to obtain the multilayer membranes. But the three more widely used in the FC area continue to be hot pressing, casting and dip coating. Hot pressing is the simplest route, which allows for the possibility of using commercial extruded membranes that usually have higher proton conductivity. Although, in this method the only bond that is formed between the layers is mechanical, so under severe environmental conditions (inside the fuel cell systems where they would face continuous expansion and compression) there is a possibility of delamination of the layers. On the other hand, during casting the interaction between the layers is mechanical as well as chemical, which makes the bond stronger, thus,

reducing the chances of delamination. However, the choice of solvent is very crucial in this process. Care needs to be taken such that the solvent of one layer does not damage/dissolve the underlying layer. Moreover, unlike hot pressing, casting excludes the possibility of using extruded membranes, which is a clear disadvantage since extruded membranes usually have better mechanical proprieties. Alternatively, dip coating brings in the prospect of achieving extremely thin layers and generating a final membrane with a large number of bi-layers, even 20 or 50. Having a large number of layers on the side will help block and minimise the dissolution of the highly sulphonated and hydrophilic polymers that would otherwise dissolve in water. Another advantage of this process is that any change in the dimensions of the inner layers will be minimised dramatically, thus decreasing the wash out rate. The only major requirement of this procedure is that the base membrane must have high mechanical strength in order to endure repeated dipping. Table 6 summarises advantages and disadvantages of these three methods.

Table 7: Routes to obtain a multilayer membrane.

Method	***Advantages***	***Disadvantages***
Hot Pressing	✓ Physical interaction between layers ✓ Fast method ✓ Solvent free ✓ Can use extruded membrane	✓ Delamination
Solvent Casting	✓ Chemical interaction between layers. ✓ No delamination ✓ Can use polymers with low mechanical strength.	✓ Use of solvents ✓ No extruded membranes
Dip Coating	✓ Chemical interaction between layers ✓ No delamination ✓ Thinner layers ✓ Allows large no. of bi-layers.	✓ Only base membrane can be extruded ✓ High strength base membrane needed.

3.4. Other Methods for Multilayer Preparation

While the three methods listed above seem to be the most commonly used preparation methods for multilayer membrane, many novel methods have also been explored by researchers in the last few years in an attempt to improve interlayer interactions, combine more polymers together and to make the multilayering process faster and more efficient. To develop a self-humidifying membrane Zhu*, et al.* [133] prepared a composite multilayer membrane where the central layer was a porous polytetrafluoroethylene (PTFE) impregnated with Nafion and the external layers consisting of Nafion and Pt-SiO_2 were sprayed on. The total thickness of the three-layer membrane was 20 µm. This particular membrane can be compared with the transitional membrane reported by Lu *et al.* [24] (discussed in section 2.1 – Organic fillers). The membrane developed by Lu *et al.* is not specifically named or reported as multilayer, but it has the same initial idea of a PTFE layer. The main difference between the two studies is the clear proposal of a multilayer membrane in the work reported by Zhu et al, while Lu *et al.* do not define their work as multilayer and the layers are not completely distinct. Li*, et al.* [134] also developed a multilayer (3 layer) membrane by spin-coating, in which external layers were a blend of poly(o-cresyl glycidyl ether)-co-formaldehyde and polyethylenimine and the inner layer was made of inorganic phosphosilicate. This ultra-thin membrane had a total thickness of 500 nm and showed a proton conductivity of 10^{-3} S cm^{-1}. The method used in this study is not widely used because there are only a limited number of polymers which would form a homogenous layer by this process. It would be particularly difficult to obtain a

homogeneous layer when one of the layers has to be sprayed on and the inner membrane is a composite material. Lu*, et al.* [135] developed a multilayer membrane, in which the inner layer was referred to as a *meso*-Nafion which was impregnated with phosphotungstic acid (HPW) and had two external layers of Nafion. The name meso-Nafion was used by authors for a Nafion with highly ordered mesoporous structure in which the HPW is stabilised. According to the authors, the HPW, due to its highly acidic nature, is capable of conducting the protons even under very low humidity conditions. The two external blocking layers of Nafion were sprayed on the inner layer surface, resulting in a total thickness of 100 µm. The authors achieved higher proton conductivity than Nafion 1135 due to the higher water uptake by the inner membrane. The performance in a PEFC single cell test was reported to be superior to that of the Nafion and was attributed to the higher proton conductivity and water uptake of HPW. The authors reported that the HPW multilayer structure effectively reduced the problem of leaching commonly associated with HPW membranes. The in-situ PEFC testing also revealed that the multilayer membrane had a significantly low degradation rate when operated at reduced humidity and elevated temperatures of 120 °C. The spray coating method used here to obtain the membrane layers was extensively detailed in the work published by Tang*, et al.* [136], describing that this method is faster and more efficient than solution casting, dip coating or any other method. The layers in the study were made of polyacrylic acid and poly(ethyleneimine) which were alternately sprayed on to a polyacrylonitrile. Although not all polymers can be sprayed on a porous substrate, this method can be very efficient and may produce considerably thinner membranes compared to most other methods. The spray coating method could be of interest when looking at industrial scale production of multilayer membranes as it can be both cost effective and time efficient.

4. Conclusions and Perspective

Various different composites based on organic as well as inorganic fillers have been reported extensively for use in IT-PEFC to overcome the problems faced by Nafion under high temperature and low humidity conditions. Composites membranes are certainly the next step forward to use Nafion-like membranes in IT-PEFC/DMFC environment. The use of hydrophilic fillers increases the water uptake leading to higher proton conductivity of the membrane. It also helps in the stability of the membrane and provides a tortuous path to the fuel. While SiO_2 and TiO_2 based fillers have been researched heavily in the last decade or so with some very interesting results, the search for other fillers and fresh combinations of filler and polymer materials continues in the bid to make the PEM more durable and efficient. The methods used to develop composite membranes are very well known since they are polymer matrix with loadings. Studies reported on the use of graphene oxide and carbon nanotubes as fillers and as Nafion free membranes show these to be promising materials for PEM applications especially because they provide increased mechanical strength. Chemical modifications of GO such as carboxylation and sulphonation have been carried out enabling further improvement of the desired properties such as increased proton conductivity along with its inherent property as an electronic insulator. However, despite the volume of work reported with this material there are still quite a few parameters like water content in GO, carbon to oxygen ratio, degree of sulphonation as well as the percentage of GO as a filler which need to be inspected and investigated extensively in order to understand its behaviour as a filler. Studies on the use of ionic liquids as fillers have highlighted their potential for use in IT-PEFC and these too are slowly gaining momentum. It would also be interesting to see if more than one filler could be effectively used in composite membranes to generate membranes with multiple attributes, which may

be suitable and effective under variable conditions. This would however, require detailed studies on the role of various functional groups that such fillers (like GO and ionic liquid) possess. Functional groups like sulphonic acids and phosphoric acid have long been known to play important role in water retention and enhancing proton conductivity. Developing an understanding of the roles and interactions of functional groups (like carboxyl, hydroxyl), present in fillers like GO, with the functional groups present in the polymers would be vital for all future membranes.

On the other hand, recent studies on multilayer membranes have been mainly focussed on DMFC. However, some successful studies have also been reported for use in PEFC, the trend is likely to generate more research interest for DMFC and IT-PEFC as the concept has been quite successful in its previous applications. The multilayer concept is of particular importance for application in IT-PEFC where there is an acute requirement for membranes, which are more tolerant towards higher temperature and low humidity conditions compared to the existing industry standard materials like Nafion. The hybrid multilayer concepts like the use of two external Nafion or other sturdy polymer layers on a sulphonated inner membrane would help strengthen its structure allowing the use of the best properties of each material. The external layers prevent the inner layer from being washed out or losing its mechanical resistance if it swells too much and help maintain its proton conductivity under more testing conditions. The use of novel polymer and filler combinations along with inventive and innovative layering techniques could prove to be a paradigm shift in the field of low temperature fuel cell membrane development. The next step for multilayer membranes development could be to combine both composite and multilayer concepts, which can offer the advantages of both (such as reduced fuel crossover

due to use of composite filler membrane layer and increased proton conductivity from the sulphonated polymer) while minimising the disadvantages associated with highly sulphonated membranes.

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References

[1] B. Sorensen, Hydrongen and Fuel Cells, Elsevier Ltda, 2012.

[2] S.J. Peighambardoust, S. Rowshanzamir, M. Amjadi, International Journal of Hydrogen Energy, 35 (2010) 9349-9384.

[3] J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Song, T. Navessin, Z. Shi, D. Song, H. Wang, D.P. Wilkinson, Z.-S. Liu, S. Holdcroft, Journal of Power Sources, 160 (2006) 872-891.

[4] Y. Wang, K.S. Chen, J. Mishler, S.C. Cho, X.C. Adroher, Applied Energy, 88 (2011) 981-1007.

[5] J. Larmine, A. Dicks, Fuel Cell System Explained, John Wiley & Sons, 2003.

[6] D.H. Kim, H.S. Park, S.J. Seo, J.S. Park, S.H. Moon, Y.W. Choi, Y.S. Jiong, M.S. Kang, Journal of colloid and interface science, 416 (2014) 19-24.

[7] P. Millet, D. Dragoe, S. Grigoriev, V. Fateev, C. Etievant, International Journal of Hydrogen Energy, 34 (2009) 4974-4982.

[8] F. Fadhillah, S.M.J. Zaidi, Z. Khan, M.M. Khaled, F. Rahman, P.T. Hammond, Desalination, 318 (2013) 19-24.

[9] S. Bose, T. Kuila, T.X.H. Nguyen, N.H. Kim, K.-t. Lau, J.H. Lee, Progress in Polymer Science, 36 (2011) 813-843.

[10] E. Spohr, Journal of Computer-Aided Materials Design, 14 (2008) 253-258.

[11] H. Sun, Z. Sun, Y. Wu, International Journal of Hydrogen Energy, 37 (2012) 12821-12826.

[12] H. Zhang, P.K. Shen, Chem Rev, 112 (2012) 2780-2832.

[13] T. Yoshida, T. Tokumasu, The Electrochemical Society, 33 (2010) 1055-1065.

[14] U. Reimer, B. Schumacher, W. Lehnert, Journal of The Electrochemical Society, 162 (2014) F153-F164.

[15] K. Angjeli, I. Nicotera, M. Baikousi, A. Enotiadis, D. Gournis, A. Saccà, E. Passalacqua, A. Carbone, Energy Conversion and Management, 96 (2015) 39-46.

[16] F.J. Pinar, P. Cañizares, M.A. Rodrigo, D. Úbeda, J. Lobato, Journal of Power Sources, 274 (2015) 177-185.

[17] K. Scott, C. Xu, X. Wu, Wiley Interdisciplinary Reviews: Energy and Environment, 3 (2014) 24-41.

[18] J. Wu, X.Z. Yuan, J.J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, Journal of Power Sources, 184 (2008) 104-119.

[19] X.-Z. Yuan, H. Li, S. Zhang, J. Martin, H. Wang, Journal of Power Sources, 196 (2011) 9107-9116.

[20] K.D. Kreur, S.J. Paddison, E. Spohr, M. Schuster, Chemical Reviews, 104 (2004) 4637−4678.

[21] S. Feng, G.A. Voth, The journal of physical chemistry. B, 115 (2011) 5903-5912.

[22] B. Wu, M. Zhao, W. Shi, W. Liu, J. Liu, D. Xing, Y. Yao, Z. Hou, P. Ming, J. Gu, Z. Zou, International Journal of Hydrogen Energy, (2014).

[23] B.-Y. Wang, C.K. Tseng, C.-M. Shih, Y.-L. Pai, H.-P. Kuo, S.J. Lue, Journal of Membrane Science, 464 (2014) 43-54.

[24] S. Lu, R. Xiu, X. Xu, D. Liang, H. Wang, Y. Xiang, Journal of Membrane Science, 464 (2014) 1-7.

[25] L. Wang, B.L. Yi, H.M. Zhang, Y.H. Liu, D.M. Xing, Z.G. Shao, Y.H. Cai, Journal of Power Sources, 167 (2007) 47-52.

[26] H. Bai, W.W. Ho, Polymer International, 60 (2010) 26-41.

[27] C. Iojoiu, F. Chabert, M. Maréchal, N.E. Kissi, J. Guindet, J.Y. Sanchez, Journal of Power Sources, 153 (2006) 198-209.

[28] H. Zhang, P.K. Shen, Chemical Society reviews, 41 (2012) 2382-2394.

[29] Y.-L. Liu, Polymer Chemistry, 3 (2012) 1373.

[30] B. Smitha, S. Sridhar, A.A. Khan, Journal of Membrane Science, 259 (2005) 10-26.

[31] N. Cele, S.S. Ray, in: Macromolecular Materials and Engineering, 2009, pp. 719–738.

[32] A. Donnadio, M. Casciola, M.L. Di Vona, M. Tamilvanan, in: Journal of Power Sources, 2012, pp. 145-150.

[33] J.-y. Park, T.-H. Kim, K.H. Joong, J.-H. Choi, Y.T. Hong, in: Internationall Journal of Hydrogen Energy, 2012, pp. 2603-2613.

[34] M.-S. Jun, Y.-W. Choi, J.-D. Kim, Journal of Membrane Science, 396 (2012) 32-37.

[35] A.L.A. Silva, I. Takase, R.P. Pereira, A.M. Rocco, European Polymer Journal, 44 (2008) 1462-1474.

[36] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Chemical Materials, 15 (2003) 4896-4915.

[37] M. Ahmed, I. Dincer, International Journal of Energy Research, 35 (2011) 1213-1228.

[38] H. Li, G. Zhang, J. Wu, C. Zhao, Q. Jia, C.M. Lew, L. Zhang, Y. Zhang, M. Han, J. Zhu, Journal of Power Sources, 195 (2010) 8061-8066.

[39] A. Alvarez, C. Guzmán, S. Rivas, L.A. Godinez, A. Saccà, A. Carbone, E. Passalacqua, L.G. Arriaga, J. Ledesma-García, International Journal of Hydrogen Energy, (2014).

[40] H.-L. Lin, T.L. Yu, L.-N. Huang, L.-C. Chen, K.-S. Shen, G.-B. Jung, Journal of Power Sources, 150 (2005) 11-19.

[41] H.-L. Lin, S.-H. Wang, Journal of Membrane Science, 452 (2014) 253-262.

[42] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chemical Reviews, 104 (2004) 4587−4612.

[43] X. Wu, K. Scott, Fuel Cells, 13 (2013) 1138-1145.

[44] P.S. Mishra, J.N. Solanki, Z.V.P. Murthy, Crystal Research and Technology, 48 (2013) 969-976.

[45] P. Zapata, J.-H. Lee, J.C. Meredith, Journal of Applied Polymer Science, 124 (2012) E241-E250.

[46] C.-M. Chang, H.-Y. Li, J.-Y. Lai, Y.-L. Liu, RSC Advances, 3 (2013) 12895.

[47] K.T. Adjemian, S.J. Lee, S. Srinivasan, J. Benziger, A.B. Bocarsly, in: Journal of The Electrochemical Society, 2002, pp. A256-A261.

[48] C.-C. Ke, X.-J. Li, S.-G. Qu, Z.-G. Shao, B.-L. Yi, Polymers for Advanced Technologies, 23 (2012) 92-98.

[49] J.-Y. Kim, Y.-H. Ohn, K.-J. Ihn, C. Lee, Journal of Applied Polymer Science, 119 (2011) 2002-2009.

[50] H.S. Thiam, W.R.W. Daud, S.K. Kamarudin, A.B. Mohamad, A.A.H. Kadhum, K.S. Loh, E.H. Majlan, International Journal of Hydrogen Energy, 38 (2013) 9474-9483.

[51] C.-H. Tsai, F.-L. Yang, C.-H. Chang, Y.W. Chen-Yang, International Journal of Hydrogen Energy, 37 (2012) 7669-7676.

[52] S.J. Peighambardoust, S. Rowshanzamir, M.G. Hosseini, M. Yazdanpour, International Journal of Hydrogen Energy, 36 (2011) 10940-10957.

[53] M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, Z. Ogumi, Electrochimica Acta, 51 (2006) 5746-5753.

[54] A. Collier, H. Wang, X. Ziyuan, J. Zhang, D. Wilkinson, International Journal of Hydrogen Energy, 31 (2006) 1838-1854.

[55] Y. Devrim, Journal of Applied Polymer Science, (2014).

[56] G. Zhang, J. Jiang, J. Liu, Journal of Wuhan University of Technology-Mater. Sci. Ed., 26 (2011) 417-421.

[57] F. Lufrano, V. Baglio, O. Di Blasi, P. Staiti, V. Antonucci, A.S. Arico, Physical chemistry chemical physics : PCCP, 14 (2012) 2718-2726.

[58] P. Mustarelli, A. Carollo, S. Grandi, E. Quartarone, C. Tomasi, S. Leonardi, A. Magistris, Fuel Cells, 7 (2007) 441-446.

[59] Y. Devrim, S. Erkan, N. Baç, I. Eroglu, International Journal of Energy Research, 37 (2013) 435-442.

[60] G. Sangeetha Rani, M.K. Beera, G. Pugazhenthi, Journal of Applied Polymer Science, 124 (2012) E45-E56.

[61] Y. Zhai, H. Zhang, J. Hu, B. Yi, Journal of Membrane Science, 280 (2006) 148-155.

[62] L. Schlagenhauf, F. Nüesch, J. Wang, Fibers, 2 (2014) 108-127.

[63] C. Oueiny, S. Berlioz, F.-X. Perrin, Progress in Polymer Science, 39 (2014) 707-748.

[64] S. Jandial, P. Jindal, International Journal of Research in Advent Technology, 2 (2014) 2321-9637.

[65] E.T. Thostenson, Z. Ren, T.-W. Chou, Composites Science and Technology, 61 (2001) 1899–1912.

[66] R. Kannan, P.P. Aher, T. Palaniselvam, S. Kurungot, U.K. Kharul, V.K. Pillai, The Journal of Physical Chemistry Letters, 1 (2010) 2109–2113.

[67] M.S. Asgari, M. Nikazar, P. Molla-abbasi, M.M. Hasani-Sadrabadi, International Journal of Hydrogen Energy, 38 (2013) 5894-5902.

[68] D. Jiang, V. Cooper, S. Dai, Nano Letters, 9 (2009) 4019-4024.

[69] Y. Sun, G. Shi, in: Journal of Polymer Science, 2013, pp. 231–253.

[70] Y.-S. Ye, C.-Y. Tseng, W.-C. Shen, J.-S. Wang, K.-J. Chen, M.-Y. Cheng, J. Rick, Y.-J. Huang, F.-C. Chang, B.-J. Hwang, Journal of Materials Chemistry, 21 (2011) 10448.

[71] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, Chemical Society reviews, 39 (2010) 228-240.

[72] L. Staudenmaier, Berichte der deutschen chemischen Gesellschaft, 31 (1898) 1481-1287.

[73] Q. Tang, Z. Zhou, Z. Chen, Nanoscale, 5 (2013) 4541-4583.

[74] M. Pumera, Electrochemistry Communications, 36 (2013) 14-18.

[75] N.-F. Chiu, T.-Y. Huang, H.-C. Lai, in: M. Aliofkhazraei (Ed.) Advances in Graphene Science, 2013.

[76] B.G. Choi, Y.S. Huh, Y.C. Park, D.H. Jung, W.H. Hong, H. Park, in: Carbon, 2012, pp. 5395-5402.

[77] H.-C. Chien, L.-D. Tsai, C.-P. Huang, C.-y. Kang, J.-N. Lin, F.-C. Chang, in: International Journal of Hydrogen Energy, 2013, pp. 13792-13801.

[78] H. Zarrin, H. Drew, Y. Jun, Z. Chen, M. Fowler, in: The Journal of Physical Chemistry C, 2011, pp. 20774-20781.

[79] Y.-C. Cao, C. Xu, X. Wu, X. Wang, L. Xing, K. Scott, in: Journal of Power Sources, 2011, pp. 8377-8382.

[80] Y. Heo, H. Im, J. Kim, in: Journal of Membrane Science, 2013, pp. 11-22.

[81] Z. Jiang, X. Zhao, Y. Fu, M. Manthiram, in: Journal of Materials Chemistry, 2012.

[82] C.W. Lin, Y.S. Lu, in: Journal of Power Sources, 2013, pp. 187-194.

[83] R. Kumar, C. Xu, K. Scott, RSC Advances, 2 (2012) 8777-8782.

[84] J.I. Paredes, S. Villar-Rodil, A. Martı´nez-Alonso, J.M.D. Tascon, Langmuir : the ACS journal of surfaces and colloids, 24 (2008) 10560-10564.

[85] D.C. Lee, H.N. Yang, S.H. Park, W.J. Kim, Journal of Membrane Science, 452 (2014) 20-28.

[86] B.G. Choi, J. Hong, Y.C. Park, D.H. Jung, W.H. Hong, P.T. Hammnond, H.S. Park, ACS Nano, 5 (2011) 5167–5174.

[87] L.-N. Huang, L.-C. Chen, T.L. Yu, H.-L. Lin, Journal of Power Sources, 161 (2006) 1096-1105.

[88] L.-C. Chen, T.L. Yu, H.-L. Lin, S.-H. Yeh, Journal of Membrane Science, 307 (2008) 10-20.

[89] J.C. Padilha, J. Basso, L.G. da Trindade, E.M.A. Martini, M.O. de Souza, R.F. de Souza, Journal of Power Sources, 195 (2010) 6483-6485.

[90] C. Xu, X. Liu, J. Cheng, K. Scott, Journal of Power Sources, 274 (2015) 922-927.

[91] S.-Y. Lee, T. Yasuda, M. Watanabe, Journal of Power Sources, 195 (2010) 5909-5914.

[92] R.S. Malik, P. Verma, V. Choudhary, Electrochimica Acta, 152 (2015) 352-359.

[93] S. Liu, L. Zhou, P. Wang, F. Zhang, S. Yu, Z. Shao, B. Yi, ACS applied materials & interfaces, 6 (2014) 3195-3200.

[94] M.C. Buzzeo, R.G. Evans, R.G. Compton, Chemphyschem : a European journal of chemical physics and physical chemistry, 5 (2004) 1106-1120.

[95] M. Armand, F. Endres, D.R. Mac.Farlane, H. Ohno, B. Scrosati, Nature Materials, 8 (2009) 9.

[96] W. Shan, P. Bacchin, P. Aimar, M.L. Bruening, V.V. Tarabara, Journal of Membrane Science, 349 (2010) 268-278.

[97] S.U. Hong, R. Malaisamy, M.L. Bruening, Langmuir : the ACS journal of surfaces and colloids, 23 (2007).

[98] C. Sheng, S. Wijeratne, C. Cheng, G.L. Baker, M.L. Bruening, Journal of Membrane Science, (2014).

[99] L. Ouyang, R. Malaisamy, M.L. Bruening, Journal of Membrane Science, 310 (2008) 76-84.

[100] B.W. Stanton, J.J. Harris, M.D. Miller, M.L. Bruening, Langmuir : the ACS journal of surfaces and colloids, 19 (2003).

[101] R. Malaisamy, M.L. Bruening, Langmuir : the ACS journal of surfaces and colloids, 21 (2005).

[102] S. Mulyati, R. Takagi, A. Fujii, Y. Ohmukai, H. Matsuyama, Journal of Membrane Science, 431 (2013) 113-120.

[103] B. Yang, A. Manthiram, Electrochemistry Communications, 6 (2004) 231-236.

[104] S.-L. Chen, A.B. Bocarsly, J. Benzinger, in: Journal of Power Sources, 2005, pp. 27-33.

[105] A.Z. Peng, A. Morin, P. Huguet, Y. Lanteri, S. Deabate, Physical Chemistry Chemical Physics, (2014).

[106] Q.X. Wu, T.S. Zhao, R. Chen, L. An, Applied Energy, 106 (2013) 301-306.

[107] W. Gao, G. wu, M.T. Janicke, D.A. Cullen, R. Mukundan, J.K. Baldwin, E.L. Brosha, C. Galande, P.M. Ajayan, K.L. More, A.M. Dattelbaum, P. Zelany, Angewandte Chemie, 126 (2014) 3662 –3667.

[108] W. Li, A. Manthiram, Journal of Power Sources, 195 (2010) 962-968.

[109] S.P. Jiang, H. Tang, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 407 (2012) 49-57.

[110] A.A. Argun, J.N. Ashcraft, P.T. Hammond, Advanced Materials, 20 (2008) 1539-1543.

[111] T. Yang, S.X. Zhang, Y. Gao, F.C. Ji, T.W. Liu, The Open Fuel Cells Journal, 1 (2008) 4-8.

[112] Q.T. Luo, H.M. Zhang, J. Chen, D.J. You, C.X. Sun, Y. Zhang, Journal of Membrane Science, 325 (2008) 553-558.

[113] M. Marrony, J. Roziere, D.J. Jones, A. Lindheimer, Fuel Cells, 5 (2005).

[114] X. Li, Y. Song, Z. Liu, P. Feng, S. Liu, Y. Yu, Z. Jiang, B. Liu, High Performance Polymers, 26 (2013) 106-113.

[115] J.-R. Lee, J.-H. Won, K.-S. Yoon, Y.T. Hong, S.-Y. Lee, International Journal of Hydrogen Energy, 37 (2012) 6182-6188.

[116] M.M. Hasani-Sadrabadi, E. Dashtimoghadam, N. Mokarram, F.S. Majedi, K.I. Jacob, Polymer, 53 (2012) 2643-2651.

[117] R. Padmavathi, R. Karthikumar, D. Sangeetha, Electrochimica Acta, 71 (2012) 283-293.

[118] M.M. Hasani-Sadrabadi, E. Dashtimoghadam, F.S. Majedi, S. Hojjati Emami, H. Moaddel, International Journal of Hydrogen Energy, 36 (2011) 6105-6111.

[119] L. Wang, B.L. Yi, H.M. Zhang, D.M. Xing, Polymers for Advanced Technologies, 19 (2008) 1809-1815.

[120] L. Wang, B.L. Yi, H.M. Zhang, Y.H. Liu, D.M. Xing, Z.G. Shao, Y.H. Cai, Journal of Power Sources, 164 (2007) 80-85.

[121] C.-C. Lin, W.-F. Lien, Y.-Z. Wang, H.-W. Shiu, C.-H. Lee, Journal of Power Sources, 200 (2012) 1-7.

[122] S. Zhong, X. Cui, C. Sun, S. Dou, W. Liu, Solid State Ionics, 227 (2012) 91-95.

[123] T. Yuan, L. Pu, Q. Huang, H. Zhang, X. Li, H. Yang, Electrochimica Acta, 117 (2014) 393-397.

[124] W. Liu, S. Wang, M. Xiao, D. Han, Y. Meng, Chem Commun (Camb), 48 (2012) 3415-3417.

[125] S. Li, S. Zhang, Q. Zhang, G. Qin, Chem Commun (Camb), 48 (2012) 12201-12203.

[126] C. Zhao, H. Lin, Q. Zhang, H. Na, International Journal of Hydrogen Energy, 35 (2010) 10482-10488.

[127] S. Yılmaztürk, H. Deligöz, M. Yılmazoğlu, H. Damyan, F. Öksüzömer, S.N. Koç, A. Durmuş, M.A. Gürkaynak, Journal of Membrane Science, 343 (2009) 137-146.

[128] M. Yang, S. Lu, J. Lu, S.P. Jiang, Y. Xiang, Chem Commun (Camb), 46 (2010) 1434-1436.

[129] H.D. Son, M.S. Cho, J.D. Nam, S.M. Cho, C.H. Chung, H.G. Choi, Y. Lee, Journal of Power Sources, 163 (2006) 66-70.

[130] H. Lin, C. Zhao, W. Ma, H. Li, H. Na, International Journal of Hydrogen Energy, 34 (2009) 9795-9801.

[131] H. Lin, C. Zhao, W. Ma, H. Li, H. Na, Journal of Membrane Science, 345 (2009) 242-248.

[132] M.A. Smit, A.L. Ocampo, M.A. Espinosa-Medina, P.J. Sebastián, Journal of Power Sources, 124 (2003) 59-64.

[133] X.B. Zhu, H.M. Zhang, Y.M. Liang, Y. Zhang, B.L. Yi, Electrochemical and Solid-State Letters, 9 (2006) A49-A52.

[134] H. Li, M. Ai, F. Jiang, H. Tu, Q. Yu, Solid State Ionics, 190 (2011) 25-29.

[135] J.L. Lu, Q.H. Fang, S.L. Li, S.P. Jiang, Journal of Membrane Science, 427 (2013) 101-107.

[136] H. Tang, G. Zhang, S. Ji, AIChE Journal, 59 (2013) 250-257.

[137] Q. Zhao, Q.F. An, Y. Ji, J. Qian, C. Gao, Journal of Membrane Science, 379 (2011) 19-45.

[138] D.C. Lee, H.N. Yang, S.H. Park, K.W. Park, W.J. Kim, in: Journal of Membrane Science, 2015, pp. 254-262.

[139] K. Ketpang, B. Son, D. Lee, S. Shanmugam, in: Journal of Membrane Science, 2015, pp. 154-165.

[140] R.N. Jana, B. Maity, S. Mallick, A. Majumdar, P. Singh, in: Indian Chemical Engineer, 2015, pp. 103-114.